Battery Separators

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1. Introduction and Scope

Many advances have been made in battery technology in recent years, both through continued improvement of specific electrochemical systems and through the development and introduction of new

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battery chemistries. Nevertheless, there is still no one "ideal" battery that gives optimum performance under all operating conditions. Similarly, there is no one separator that can be considered "ideal" for all battery chemistries and geometries.

A separator is a porous membrane placed between electrodes of opposite polarity, permeable to ionic flow but preventing electric contact of the electrodes. A variety of separators have been used in batteries over the years. Starting with cedar shingles and sausage casing, separators have been manufactured from cellulosic papers and cellophane to nonwoven fabrics, foams, ion exchange membranes, and microporous flat sheet membranes made from polymeric materials. As batteries have become more sophisticated, separator function has also become more demanding and complex.

Separators play a key role in all batteries. Their main function is to keep the positive and negative electrodes apart to prevent electrical short circuits and at the same time allow rapid transport of ionic charge carriers that are needed to complete the circuit during the passage of current in an electrochemical cell.[1,2] They should be very good electronic insulators and have the capability of conducting ions by either intrinsic ionic conductor or by soaking electrolyte. They should minimize any processes that adversely affect the electrochemical energy efficiency of the batteries.

Very little work (relative to research of electrode materials and electrolytes) is directed toward characterizing and developing new separators. Similarly, not much attention has been given to separators in publications reviewing batteries.[1−10] A number of reviews on the on cell fabrication, their performance, and application in real life have appeared in recent years, but none have discussed separators in detail. Recently a few reviews have been published in both English and Japanese which discuss different types of separators for various batteries.[11−20] A detailed review of lead-acid and lithium-ion (li-ion) battery separators was published by Boehnstedt[13] and Spotnitz,[14] respectively, in the *Handbook of Battery Materials*. Earlier Kinoshita et al. had done a survey of different types of membranes/separators used in different electrochemical systems, including batteries.[11]

The majority of the separators currently used in batteries were typically developed as spin-offs of existing technologies. They were usually not developed specifically for those batteries and thus are not completely optimized for systems in which they are used. One positive result of adapting existing technologies is that they are produced in high volume at relatively low cost. The availability of low cost separators is an important consideration in the commercialization of batteries, because the battery industry traditionally operates with thin profit margins and relatively small research budgets.

The purpose of this paper is to describe the various types of separators based on their applications in batteries and their chemical, mechanical and electrochemical properties, with particular emphasis on separators for lithium-ion batteries. The separator requirements, properties, and characterization techniques are described with respect to lithium-ion batteries. The separators used in other batteries are only discussed briefly. Despite the widespread use of separators, a great need still exists for improving the performance, increasing the life, and reducing the cost of separators. In the following sections, an attempt is made to discuss key issues in various separators with the hope of bringing into focus present and future directions of research and development in separator technologies.

2. Battery and Separator Market

The battery industry has seen enormous growth over the past few years in portable, rechargeable battery packs. The majority of this surge can be attributed to the widespread use of cell phones, personal digital assistants (PDA's), laptop computers, and other wireless electronics. Batteries remained the mainstream source of power for systems ranging from mobile phones and PDA's to electric and hybrid electric vehicles. The world market for batteries was approximately $41 billion in 2000, which included $16.2 billion primary and $24.9 billion secondary cells.[21]

A recent study from Freedonia has predicted aggregate U.S. demand for primary and secondary batteries to climb 5.5% annually through 2007 to $14 billion. The growth will be driven by strong demand for battery-powered electronic devices like digital cameras and 3G wireless phones, and increasing production of electrical and electronic equipment. The secondary battery demand is expected to outpace the primary battery market gains through 2007 benefiting from strong growth in the use of high-drain portable electronic devices. The lead-acid batteries will account for over half of all rechargeable demand in 2007, although lithium-ion and NiMH batteries will record the strongest growth. Alkaline batteries could remain the dominant type, accounting for more than two thirds of all primary battery sales in 2007.[22]

The rechargeable battery (NiCd, NiMH, and lithium-ion) market for 2003 for portable electronics was around $5.24 billion, around 20% more then 2002. The lithium-ion battery market was around $3.8 billion (∼73%). They are now used in more than 90% of cellphones, camcorders, and portable computers, worldwide, and have also been adopted in power tools recently.[23]

The tremendous progress in lithium-ion cells is clearly visible with as much as a 2-fold increase in the volumetric and gravimetric energy density for both 18650 and prismatic cells between 1994 and 2002. In past few years the lithium-ion production has expanded to South Korea (Samsung, LG, etc.) and China (BYD, B&K, Lishen, etc.) from Japan. Several Japanese (Sanyo, Sony, MBI, NEC, etc.) and Korean (LG Chemical) manufacturers have also moved their manufacturing plants to China.[23] Japan, which controlled 94% of the global rechargeable battery market in 2000, has seen its market share drop to about 65% of the global market.[23−25] The continued growth in lithium-ion battery market has led to a strong demand for battery separators. All the

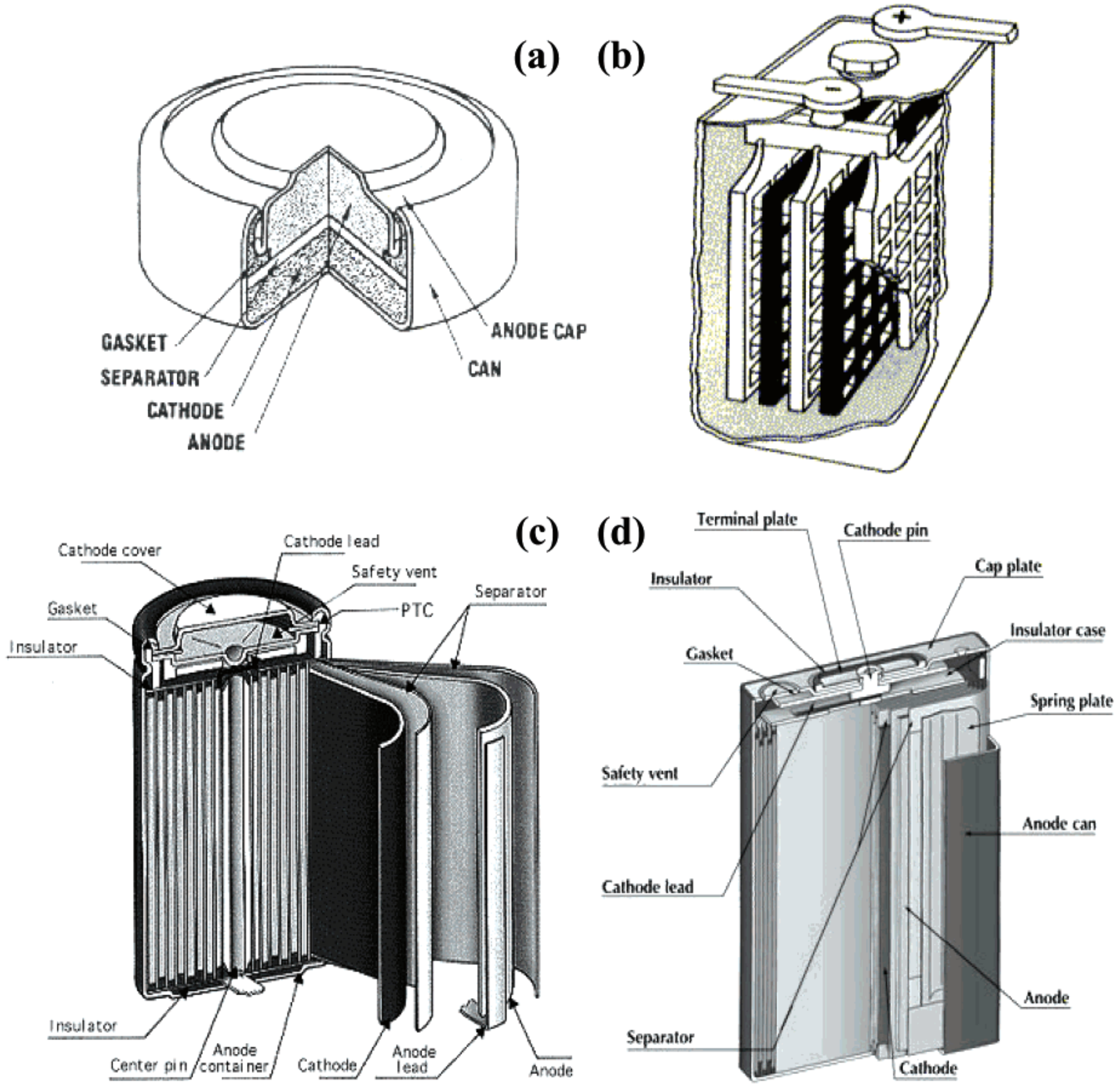

Figure 1. Typical battery configurations: (a) button cell; (b) stack lead-acid; (c) spiral wound cylindrical lithium-ion; (d) spiral wound prismatic lithium-ion.

major separator manufacturers (Celgard, Asahi, and Tonen) have either increased their capacity in 2003 or are planning to increase it in 2004.[26−28]

There is not too much information available on the battery separator market in the literature. It is estimated that about 30% of the rechargeable lithium battery market or $1.5 billion is the size of the battery materials or components market. Battery separators for lithium batteries are about a $330 million market within the total battery components market.[29,30] Recently, the Freedonia Group has reported that the U.S. demand for battery separators will increase to $410 million in 2007 from $237 million in 1977 and $300 million in 2002, respectively.[31,32]

3. Separator and Batteries

Batteries are built in many different shapes and configurations—button, flat, prismatic (rectangular), and cylindrical (AA, AAA, C, D, 18650, etc.). The cell components (including separators) are designed to accommodate a particular cell shape and design. The separators are either stacked between the electrodes or wound together with electrodes to form jellyrolls as shown in Figure 1. Stacked cells are generally held together by pressure from the cell container. The lithium-ion gel polymer stacked cells are prepared by bonding/laminating layers of electrodes and separators together. The separator properties should not change significantly during the bonding process. In some cases, the separators are coated to help in bonding process, thus reducing the interfacial resistance.[33−35]

In the conventional way of making spirally wound cells, two layers of separators are wound along with the positive and negative electrodes, resulting in a positive/separator/negative/separator configuration. They are wound as tightly as possible to ensure good interfacial contact. This requires the separators to be strong to avoid any contact between the electrodes through the separator. The separator also must not yield and reduce in width, or else the electrodes may contact each other. Once wound, the jellyroll is inserted into a can, and filled with electrolyte. The separator must be wetted quickly by the electrolyte to reduce the electrolyte filling time. A header is then crimped into the cell to cover the can from top. In some prismatic cells, the jellyroll is pressed at high temperatures and pressures and then inserted into thin prismatic (rectangular) cans. A typical 18650 lithium-ion cell uses around 0.07−0.09 m^2 of separator, which is approximately 4−5% of the total cell weight.[36]

4. Separator Requirements

A number of factors must be considered in selecting the best separator for a particular battery and application. The characteristics of each available separator must be weighed against the requirements and one selected that best fulfills these needs. A wide variety of properties are required of separators used in batteries. The considerations that are important and influence the selection of the separator include the following:

- Electronic insulator
- Minimal electrolyte (ionic) resistance
- Mechanical and dimensional stability
- Sufficient physical strength to allow easy handling
- Chemical resistance to degradation by electrolyte, impurities, and electrode reactants and products
- Effective in preventing migration of particles or colloidal or soluble species between the two electrodes
- Readily wetted by electrolyte
- Uniform in thickness and other properties

The order of importance of the various criteria varies, depending on the battery applications. The above list presents a broad spectrum of requirements for separators in batteries. In many applications, a compromise in requirements for the separator must generally be made to optimize performance, safety, cost, etc. For example, batteries that are characterized by small internal resistance and consume little power require separators that are highly porous and thin, but the need for adequate physical strength may require that they be thick.

In addition to the above general requirements each battery type has other requirements essential for good performance and safety. For example, separators in sealed nickel−cadmium (NiCd) and nickel−metal hydride (NiMH) batteries should be highly permeable to gas molecules for overcharge protection, the separator in lithium-ion cells should have a shutdown feature for good safety, separators for alkaline batteries should be flexible enough to be wrapped around the electrodes, and the separator for an SLI (starting, lighting and ignition) battery could also serve as a mechanical-shock cushion.

5. Separator Types

Separators for batteries can be divided into different types, depending on their physical and chemical characteristics. They can be molded, woven, nonwoven, microporous, bonded, papers, or laminates. In recent years, there has been a trend to develop solid and gelled electrolytes that combine the electrolyte and separator into a single component.

In most batteries, the separators are either made of nonwoven fabrics or microporous polymeric films. Batteries that operate near ambient temperatures usually use separators fabricated from organic materials such as cellulosic papers, polymers, and other fabrics, as well as inorganic materials such as asbestos, glass wool, and SiO_2. In alkaline batteries, the separators used are either regenerated cellulose or microporous polymer films. The lithium batteries with organic electrolytes mostly use microporous films.

For the sake of discussion, we have divided the separators into six types—microporous films, nonwovens, ion exchange membranes, supported liquid membranes, solid polymer electrolytes, and solid ion conductors. A brief description of each type of separator and their application in batteries are discussed below.

5.1. Microporous Separators

They are fabricated from a variety of inorganic, organic, and naturally occurring materials and generally contain pores that are greater than 50−100 Å in diameter. Materials such as nonwoven fibers (e.g. nylon, cotton, polyesters, glass), polymer films (e.g. polyethylene (PE), polypropylene (PP), poly(tetrafluoroethylene) (PTFE), poly(vinyl chloride) (PVC)), and naturally occurring substances (e.g. rubber, asbestos, wood) have been used for microporous separators in batteries that operate at ambient and low temperatures (<100 °C). The microporous polyolefins (PP, PE, or laminates of PP and PE) are widely used in lithium based nonaqueous batteries (section 6.1), and filled polyethylene separators in lead-acid batteries (section 7.3), respectively.

5.2. Nonwovens

Nonwovens are textile products that are manufactured directly from fibers. They are defined as a manufactured sheet, web, or matt of directionally or randomly oriented fibers, bonded by friction, and/or cohesion, and/or adhesion excluding paper and products which are woven, tufted, stichbounded incorporating binding yarns or filaments, or felted by wetmilling whether or not additionally needed. The fibers may be of natural or manmade origin. They may be staple or continuous filaments or maybe formed in situ.[37]

The macroporous fibrous matrix is either dry laid, meltblown, or wet laid. The wet laid process is very similar to the papermaking process. The fibers are bonded together by chemical or thermal bonding. The meltblown process is a binderless process and there the polymer fiber web is extruded. Typical pore sizes of the fibrous matrix vary from 1 to 100 μm.

Nonwovens are widely utilized as separators for several types of batteries. Lightweight, wet laid nonwovens made from cellulose, poly(vinyl alcohol), and other fibers have achieved considerable success as separators for popular primary alkaline cells of various sizes. The key nonwoven attributes include consistently uniform basis weight, thickness, porosity and resistance to degradation by electrolytes. Nonwovens are also successfully employed as separators in NiCd's.

Table 1. Types of Separators Used in Different Type of Secondary Lithium Batteries

battery system	type of separator	composition
lithium-ion (liquid electrolyte)	microporous	polyolefins (PE, PP, PP/PE/PP)
lithium-ion gel polymer	microporous	PVdF
	microporous	polyolefins (PE, PP, PP/PE/PP) coated with PVdF or other gelling agents
lithium-polymer (e.g. Li$-$V$_6$O$_{13}$)	polymer electrolyte	poly(ethylene oxide) with lithium salt

The materials used in nonwoven fabrics include a single polyolefin, or a combination of polyolefins, such as polyethylene (PE), polypropylene (PP), polyamide (PA), poly(tetrafluoroethylene) (PTFE), polyvinylidine fluoride (PVdF), and poly(vinyl chloride) (PVC). Nonwoven fabrics have not, however, been able to compete with microporous films in lithium-ion cells. This is most probably because of the inadequate pore structure and difficulty in making thin ($<$25 μm) nonwoven fabrics with acceptable physical properties.

5.3. Ion Exchange Membranes

These membranes are generally fabricated from polymeric materials containing pores with diameters of less than 20 Å. The transport properties of ions in these membranes are characterized by strong interactions between the permeating species and the molecular structure of the polymer. This interaction is due to the presence of ion-exchange groups in the membrane, which allows the membrane to discriminate between permeating or migrating ions by virtue of their specific charge.

Radiation grafted membranes such as Permion manufactured by RAI Research Corporation are ion-exchange membranes. Such membranes are used as battery separators in alkaline batteries. They are made from PE, PP, or Teflon-based films, which have excellent oxidation resistance and superior chemical resistance to alkali. However, they are totally impervious to electrolyte flow, and therefore, they have almost infinite resistance as a separator in this form. By using radiation grafting and cross-linking techniques, however, selected chemical species are grafted as pendant chains to the base structure of the linear polymer without altering the inert backbone. This modification imparts desirable hydrophilic properties to the films without materially impairing their excellent chemical resistance. This paper provides a very limited discussion on ion exchange membranes, as their application in batteries is very limited.

5.4. Supported Liquid Membranes

These types of separators consist of a solid matrix and a liquid phase, which is retained in the microporous structure by capillary forces. To be effective for batteries, the liquid in the microporous separator, which generally contains an organic phase, must be insoluble in the electrolyte, chemically stable, and still provide adequate ionic conductivity. Several types of polymers, such as polypropylene, polysulfone, poly(tetrafluoroethylene), and cellulose acetate, have been used for porous substrates for supported-liquid membranes. The PVdF coated polyolefin-based microporous membranes used in gel−polymer lithium-ion battery fall into this category. Gel polymer electrolytes/membranes are discussed briefly in section 6.3.

5.5. Polymer Electrolyte

Polymer electrolytes (e.g., poly(ethylene oxide), poly(propylene oxide)) have attracted considerable attention for batteries in recent years. These polymers form complexes with a variety of alkali metal salts to produce ionic conductors that serve as solid electrolytes. Their use in batteries is still limited due to poor electrode/electrolyte interface and poor room temperature ionic conductivity. Because of the rigid structure, they can also serve as the separator. Polymer electrolytes are discussed briefly in section 6.2.

5.6. Solid Ion Conductors

They serve as both separator and electrolyte. These are generally inorganic materials that are impervious barriers to gases and liquids. They allow one or more kinds of ions to migrate through their lattice when a potential gradient or a chemical gradient is present. These types of separators are beyond the scope of this article.

6. Separator for Nonaqueous Batteries

All lithium based batteries use nonaqueous electrolytes because of the reactivity of lithium in aqueous solution and because of the electrolyte's stability at high voltage. The majority of these cells use microporous membranes made of polyolefins. In some cases, nonwovens made of polyolefins are either used alone or with microporous separators. This section will mainly focus on separators used in secondary lithium batteries followed by a brief summary of separators used in lithium primary batteries.

Lithium secondary batteries can be classified into three types, a liquid type battery using liquid electrolytes, a gel type battery using gel electrolytes mixed with polymer and liquid, and a solid type battery using polymer electrolytes. The types of separators used in different types of secondary lithium batteries are shown in Table 1. The liquid lithium-ion cell uses microporous polyolefin separators while the gel polymer lithium-ion cells either use a PVdF separator (e.g. PLION cells) or PVdF coated microporous polyolefin separators. The PLION cells use PVdF loaded with silica and plasticizer as separator. The microporous structure is formed by removing the plasticizer and then filling with liquid electrolyte. They are also characterized as plasticized electrolyte. In solid polymer lithium-ion cells, the solid electrolyte acts as both electrolyte and separator.

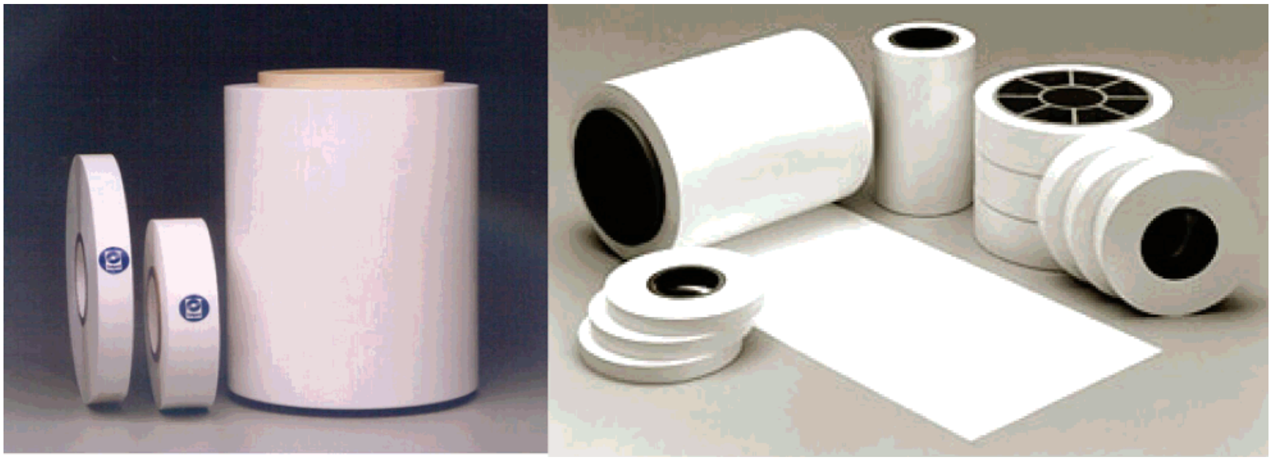

Figure 2. Polyolefin separators used in lithium-ion batteries.

6.1. Lithium Ion

The past decade has seen significant advances in the ambient temperature lithium battery technology. Lithium-ion batteries are the preferred power source for most portable electronics because of their higher energy density, longer cycle life, and higher operational voltage as compared to NiCd and NiMH systems. In 2002, 66% of the total rechargeable battery market for mobile IT and communication devices used lithium-based batteries and the rest used nickel-based batteries.[38,39]

A typical lithium-ion cell consists of a positive electrode composed of a thin layer of powdered metal oxide (e.g., $LiCoO_2$) mounted on aluminum foil and a negative electrode formed from a thin layer of powdered graphite, or certain other carbons, mounted on a copper foil. The two electrodes are separated by a porous plastic film soaked typically in $LiPF_6$ dissolved in a mixture of organic solvents such as ethylene carbonate (EC), ethyl methyl carbonate (EMC), or diethyl carbonate (DEC). In the charge/discharge process, lithium ions are inserted or extracted from the interstitial space between atomic layers within the active materials.

Sony's introduction of the rechargeable lithium-ion battery in the early 1990s precipitated a need for new separators that provided not only good mechanical and electrical properties but also added safety through a thermal shutdown mechanism. Although a variety of separators (e.g., cellulose, nonwoven fabric, etc.) have been used in different type of batteries, various studies on separators for lithium-ion batteries have been pursued in past few years as separators for lithium-ion batteries require different characteristics than separators used in conventional batteries.

A novel microporous separator using polyolefins has been developed and used extensively in lithium-ion batteries since it is difficult for conventional separator materials to satisfy the characteristics required in lithium-ion batteries. In lithium-ion batteries two layers of separators are sandwiched between positive and negative electrodes and then spirally wound together in cylindrical and prismatic configurations. The pores of the separator are filled with ionically conductive liquid electrolyte.

Microporous polyolefin membranes (see Figure 2) in current use are thin (<30 μm) and are made of polyethylene (PE), polypropylene (PP), or laminates[40] of polyethylene and polypropylene. They are made up of polyolefins materials because they provide excellent mechanical properties, chemical stability and acceptable cost.[41,42] They have been found to be compatible with the cell chemistry and can be cycled for several hundred cycles without significant degradation in chemical or physical properties.

Commercial membranes offer pore size in the range 0.03−0.1 μm, and 30−50% porosity. The low melting point of PE enables their use as a thermal fuse. As the temperature approaches the melting point of the polymer, 135 °C for PE and 165 °C for PP, porosity is lost. The trilayer material (PP/PE/PP)[43] has been developed by Celgard where a PP layer is designed to maintain the integrity of the film, while the low melting point of PE layer is intended to shutdown the cell if an over-temperature condition is reached.[108] Asahi Kasai's flat-film membrane "Hipore" is available in thicknesses ranging from 20 μm to several hundred micrometers, and with highly uniform pore sizes ranging from 0.05 to 0.5 μm.[44] The major manufacturers of lithium-ion battery separators along with their typical products are listed in Table 2.

In recent years there have been a strong demand for higher capacity lithium-ion cells because of the strong growth in portable electronics. One way to achieve higher capacity is by reducing the thickness of separators. The battery manufacturers have started using 20 and 16 μm separators in higher capacity (>2.0 A h) cylindrical cells, and 9 μm separators in lithium-ion gel polymer cells.

Nonwoven materials have also been developed for lithium-ion cells but have not been widely accepted, in part due to the difficulty in fabricating thin materials with good uniformity and high strength.[14] Nonwoven separators have been used in button cells and bobbin cells when thicker separators and low discharge rates are acceptable.

6.1.1. Separator Development

The process for making lithium-ion battery separators can be broadly divided into dry[45,46] and wet[47] processes. Both processes usually employ one or more orientation steps to impart porosity and/or increase tensile strength. The dry process involves melting a polyolefin resin, extruding it into a film, thermally

Table 2. Major Manufacturers of Lithium-Ion Battery Separators along with Their Typical Products

manufacturer	structure	composition	process	trade name
Asahi Kasai	single layer	PE	wet	HiPore
Celgard LLC	single layer	PP, PE	dry	Celgard
	multilayer	PP/PE/PP	dry	Celgard
	PVdF coated	PVdF, PP, PE, PP/PE/PP	dry	Celgard
Entek Membranes	single layer	PE	wet	Teklon
Mitsui Chemical	single layer	PE	wet	
Nitto Denko	single layer	PE	wet	
DSM	single layer	PE	wet	Solupur
Tonen	single layer	PE	wet	Setela
Ube Industries	multi layer	PP/PE/PP	dry	U-Pore

Table 3. Manufacturing Process of Typical Microporous Film

process	mechanism	raw material	properties	typical membranes	manufacturers
dry process	drawing	polymer	simple process anisotropic film	PP, PE, PP/PE/PP	Celgard, Ube
wet process	phase separation	polymer + solvent	isotropic film	PE	Asahi, Tonen
		polymer + solvent + filler	large pore size high porosity	PE	Asahi

annealing it to increase the size and amount of lamella crystallites, and precisely stretching it to form tightly ordered micropores.[48−52] In this process, a row lamellar crystal structure is generated in the polymer in the initial extrusion step. This nonporous structure is highly oriented as a result of extrusion and annealing conditions. The films are then stretched to form micropores. This microporous structure is continuous throughout the bulk interior of the membrane.[53]

Polypropylene and polyethylene microporous films obtained by this method are available from Celgard[48,50,54,55] and Ube.[56] The dry process is technologically convenient because no solvents are required. However, only a uniaxial stretching method has been successful to date, and as a result, the pores are slitlike in shape and the mechanical properties of films are anisotropic. The tensile strength in the lateral direction is relatively low.

Wet process (phase inversion process)[57,58] involves mixing of hydrocarbon liquid or some other low-molecular weight substance generally with a polyolefin resin, heating and melting the mixture, extruding the melt into a sheet, orientating the sheet either in the machine direction (MD) or biaxially, and then extracting the liquid with a volatile solvent.[45,59] Separators made by the wet process are available from Asahi Kasei,[60] Tonen,[61−63] and Mitsui Chemicals[64] and more recently from Polypore/Membrana and Entek.[65] The structure and properties of the membranes can be changed by controlling the composition of the solutions and the evaporation or subtractions of solvents in the gelation and solidification processes. The separators made by wet process use ultrahigh-molecular-weight polyethylene (UHMWPE). The use of UHMWPE gives good mechanical properties as well as some degree of melt integrity.

Ihm et al. have given a nice overview of the wet process by preparing a separator with polymer blends of high-density polyethylene (HDPE) and ultrahigh molecular weight polyethylene (UHMWPE).[58] They showed that the mechanical strength and drawing characteristics are influenced by the content and the molecular weight of the UHMWPE contained in a polyolefin blending solution. The manufacturing process of typical microporous film by dry and wet process is compared in Table 3.

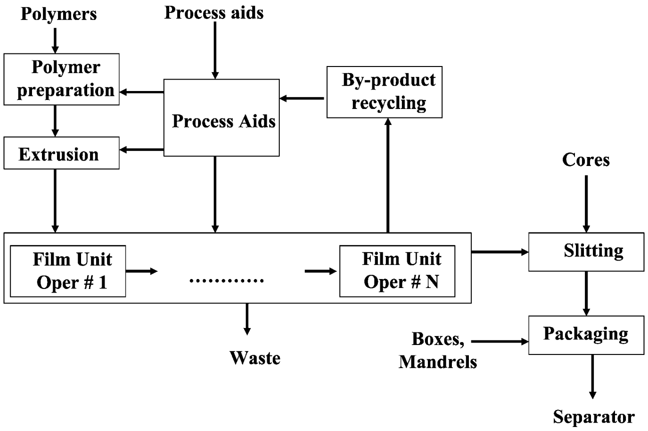

Figure 3. Generalized process for lithium-ion separator manufacturing.[66] Each step of the separator manufacturing process has online detection systems to monitor the quality of the separator.

A simplified flowchart for separator manufacturing process is shown in Figure 3.[66] The virgin polymer is prepared and mixed with processing aids (e.g., antioxidants, plasticizer, etc.) and then extruded. The extruded polymer then goes through different steps, which vary from process to process. For the dry process, it can involve film annealing and stretching, while for the wet process, it can involve solvent extraction and stretching. The finished film is then slit into required widths and packed into boxes and shipped to the battery manufacturers. With the advent of thinner separators, the film handling during manufacturing steps has become very important for the final quality of the film. Each step of the separator manufacturing process has online detection systems to monitor the quality of the separators.

Uniaxially oriented films generally have high strength in only one direction, whereas biaxially oriented films are relatively strong in both machine direction (MD) and transverse direction (TD). Although intuitively one might expect biaxially oriented films to be preferred over uniaxially oriented films,

Table 4. Typical Properties of Some Commercial Microporous Membranes

separator/properties	Celgard 2730	Celgard 2400	Celgard 2320	Celgard 2325	Asahi Hipore	Tonen Setela
structure	single layer	single layer	trilayer	trilayer	single layer	single layer
composition	PE	PP	PP/PE/PP	PP/PE/PP	PE	PE
thickness (um)	20	25	20	25	25	25
gurley (s)	22	24	20	23	21	26
ionic resistivity[a] (Ω cm^2)	2.23	2.55	1.36	1.85	2.66	2.56
porosity (%)	43	40	42	42	40	41
melt temp (°C)	135	165	135/165	135/165	138	137

[a] In 1 *M* $LiPF_6$ EC:EMC (30:70 by volume).

in practice biaxial orientation provides no performance advantage. In fact, biaxial orientation tends to introduce TD shrinkage. This shrinkage, at elevated temperatures, can allow electrodes to contact each other. The separator must have sufficient strength in the machine direction so that it does not decrease in width or break under the stress of winding. The strength in the transverse direction is not as important as that in the machine direction during the process of making spirally wound batteries. The minimum generally practical requirement for the mechanical strength of the 25-μm separator is 1000 kg/mm^2.[58]

The typical properties of some commercial microporous membranes are summarized in Table 4. Celgard 2730 and Celgard 2400 are single layer PE and PP separators, respectively, while Celgard 2320 and 2325 are trilayer separators of 20 and 25 μm thickness. Asahi and Tonen separators are single layer PE separators made by the wet process. Basic properties, such as thickness, gurley, porosity, melt temperature, and ionic resistivity are reported in Table 4. These properties are defined in section 6.1.3.

Efforts have been made to find a new route for dry process using biaxial stretching techniques for preparing polypropylene microporous films, which may have submicrometer pore sizes and narrow pore size distributions and high permeability to gases and liquids combined with good mechanical properties. The biaxially stretched polypropylene microporous films (Micpor) were made by using nonporous polypropylene films of high β-crystal content.[67] The porosity of these films can be as high as 30−40%, with an average pore size of approximately 0.05 μm. The pores on the surface were almost circular in shape compared to slitlike pores observed in uniaxial stretched samples and exhibited high permeability to fluids with good mechanical properties and almost circular pore shape with narrow pore size distribution.[68−70]

The PP/PE bilayers[40] and PP/PE/PP trilayer separators were developed by Celgard. Multilayer separators offer advantages by combining the lower melting temperature of PE with the high-temperature strength of PP. Nitto Denko has also patented a single-layer separator made from a blend of PE/PP by the dry stretch process.[71] According to the patent, the separator has microporous regions of PE and PP. On heating in an oven, the impedance of the separator increases near the melting point of PE and the impedance remains high until beyond the melting point of PP. However, battery performance data have not been presented.

Microporous polyethylene separator material composed of a combination of randomly oriented thick and thin fibrils of ultrahigh molecular weight polyethylene (UHMWPE), Solupur, manufactured by DSM Solutech, is also an interesting separator material for lithium-ion batteries. Solupur is fabricated in standard grades with base weights ranging from 7 to 16 g/m^2 and mean pore size ranging from 0.1 to 2.0 μm and a porosity of 80−90%.[72] Ooms et al. carried out a study on a series of DSM Solupur materials with different permeability. Rate capability and cycling tests of these materials were compared with commercial available separators in CR2320 type coin cells. Solupur materials showed low tortuosity, high strength and puncture resistance, excellent wettability, and good high rate capability and low-temperature performance because of its high porosity and UHMWPE structure.[73]

Recently Nitto Denko has developed a battery separator made by a wet process that had high puncture strength and high heat rupture resistance.[74] They used a polyolefin resin with a high molecular weight rubber as its main component materials and cross-linked through oxidation in air. The melt rupture temperature, as measured by thermomechnical analysis was over 200 °C in this material. They also tried cross-linking ultrahigh molecular weight polyethylene with electron-beam and ultraviolet irradiation, but this had the side effect of causing deterioration in the polyolefin including rupture of the main chains and therefore resulted in reduced strength.

ENTEK Membranes LLC has developed Teklon—a highly porous, ultrahigh molecular weight polyethylene separator for lithium-ion batteries. At the writing of this publication, the separator is available in small quantities. Pekala et al. characterized Celgard, Setela, and Teklon separators in terms of their physical, mechanical, and electrical properties.[75]

Celgard's separators are by far the best-characterized battery separators in the literature as they have been widely used in numerous battery systems. Bierenbam et al.[45] has described the process, physical and chemical properties, and end-use applications. Fleming and Taskier[76] described the use of Celgard microporous membranes as battery separators. Hoffman et al.[77] presented a comparison of PP and PE Celgard microporous materials. Callahan discussed a number of novel uses of Celgard membranes. Callahan and co-workers[98] also characterized Celgard membranes by SEM image analysis, mercury porosimetry, air permeability, and electrical resistivity, and later they characterized the puncture strength and temperature/impedance data for Celgard membranes.[40] Spotnitz et al. reported short-circuit behavior in simulated, spirally wound cells, as well as impedance/temperature behavior and thermomechanical properties.[108] Yu[78] found that a trilayer structure of PP/PE/PP Celgard microporous membranes provided exceptional puncture strength.

Nonwoven materials such as cellulosic fibers have never been successfully used in lithium batteries. This lack of interest is related to the hygroscopic nature of cellulosic papers and films, their tendency to degrade in contact with lithium metal, and their susceptibility to pinhole formation at thickness of less than 100 μm. For future applications, such as electric vehicles and load leveling systems at electric power plants, cellulosic separators may find a place because of their stability at higher temperatures when compared to polyolefins. They may be laminated with polyolefin separators to provide high-temperature melt integrity.

Asahi Chemical Industry carried out an exploratory investigation to determine the requirements for cellulose based separators for lithium-ion batteries.[79] In an attempt to obtain an acceptable balance of lithium-ion conductivity, mechanical strength, and resistance to pinhole formation, they fabricated a composite separator (39−85 μm) that consists of fibrilliform cellulosic fibers (diameter 0.5−5.0 μm) embedded in a microporous cellulosic (pore diameter: 10−200 nm) film. The fibers can reduce the possibility of separator meltdown under exposure to heat generated by overcharging or internal short-circuiting. The resistance of these films was equal to or lower than the conventional polyolefin-based microporous separators. The long-term cycling performance was also very comparable.

Pasquier et al.[80] used paper based separators in flat pouch type lithium-ion batteries and compared the performance with cells made with Celgard type polyolefin based separators. The paper separators had good wetting properties and good mechanical properties but did not provide the shutdown effect essential for large lithium-ion batteries. Their resistance was similar to polyolefin separators, and when all water traces were removed from paper, their cycling performance was similar to that of Celgard separators. The paper-based separators can be used in small flat pouch type cells where high strength and shutdown behavior is not required. For larger spherically wound cells, which require strong separators with a shutdown feature, one can never use paper-based separators.

Recently Degussa announced that they have developed Separion separators for lithium batteries by combining the characteristics of flexible polymeric separators with the advantages of chemical and thermally resistant and hydrophilic ceramic materials. Separion is produced in a continuous coating process. Ceramic materials, e.g., alumina, silica, and/or zirconia are slip coated and hardened onto a support.[81,82] According to Degussa, Separion separators have an excellent high temperature stability, superior chemical resistance, and good wettability, especially at low temperatures. They tested the performance and safety behavior of Separion separator in 18650 cells and found the performance to be comparable to that of polyolefin-based separators.[83]

The potential use of polymeric ion-exchange membranes in the next generation single-ion secondary lithium polymer batteries was shown by Sachan et al.[84,85] Conductivities exceeding 10^{-4} S/cm with transference numbers of unity were achieved for Nafion converted to the Li^+ salt form.

To obtain a thin (less than 15 μm) separator for lithium batteries, Optodot has taken a different approach of high-speed coating of a metal oxide sol−gel coating on a smooth surface followed by a delamination step to provide the free-standing separator. Using this approach, separator with thicknesses from 6 to 11 μm was made on large-scale production coating equipment.[86] They found that the sol−gel separators with a thickness in the middle of this range of 8−9 μm have the preferred combination of thinness and strength. The metal oxide sol−gel coating is water-based with no organic solvents present. The coating formulations include a polymer and a surfactant. The polymer provides improved coating rheology, mechanical strength, and other properties. The surfactant provides improved wetting properties on the substrate. The films prepared were around 11 μm thick, with 45% porosity, and were completely wettable in nonaqueous electrolyte and had a melt temperature greater than 180 °C. These films are relatively thin and should help in increasing the capacity but may not be strong enough for tightly wound cells. Moreover, the shutdown temperature of the separator seems to be very high and thus not suitable for lithium-ion batteries.

Gineste et al. carried out the grafting of hydrophilic monomers onto PP or PE separators to improve the wettability of separators used in secondary lithium batteries with a lower content of wetting agents.[87,88] They used a PP film (Celgard 2505) of 50 μm thickness after irradiating in air by electron beams with a dose ranging from 0.5 to 4 Mrad. The irradiated film was grafted by a monofunctional monomer (acrylic acid, AA), in the presence of difunctional cross-linking agent (diethylene glycol dimethacrylate, DEGDM). The separators start loosing mechanical properties, when the grafting ratio is higher than 50%.

6.1.2. Separator Requirements

In lithium-based cells, the essential function of battery separator is to prevent electronic contact, while enabling ionic transport between the positive and negative electrodes. It should be usable on high-speed winding machines and possess good shutdown properties. The most commonly used separators for primary lithium batteries are microporous polypropylene membranes. Microporous polyethylene and laminates of polypropylene and polyethylene are widely used in lithium-ion batteries.[89] These materials are chemically and electrochemically stable in secondary lithium batteries.

The general requirements[90] for lithium-ion battery separators are given below.

6.1.2.1. Thickness. The lithium-ion cells used in consumer applications use thin microporous separators (<25 μm). The separators being developed for EV/HEV applications will require thicker (~40 μm) separators. The thicker the separator, the greater the mechanical strength and the lower the probability of punctures during cell assembly but the smaller the amount of active materials that can be placed in the can. The thinner separators take up less space and permit the use of longer electrodes. This increased both capacity and, by increasing the interfacial area, rate capability. The thinness also makes it a low resistance separator.

6.1.2.2. Permeability. The separators should not limit the electrical performance of the battery under normal conditions. Typically the presence of separator increases the effective resistivity of the electrolyte by a factor of 6−7. The ratio of the resistivity of the separator filled with electrolyte divided by the resistivity of the electrolyte alone is called MacMullin number. MacMullin numbers are as high as 10−12 have been used in consumer cells.

6.1.2.3. Gurley (Air Permeability). Air permeability is proportional to electrical resistivity, for a given separator morphology. It can be used in place of electrical resistance (ER) measurements once the relationship between gurley and ER is established. The separator should have low gurley values for good electrical performance.

6.1.2.4. Porosity. It is implicit in the permeability requirement; typically lithium-ion battery separators have a porosity of 40%. Control of porosity is very important for battery separators. Specification of percent porosity is commonly an integral part of separator acceptance criteria.

6.1.2.5. Wettability. The separators should wet out quickly and completely in typical battery electrolytes.

6.1.2.6. Electrolyte Absorption & Retention. A separator should be able to absorb and retain electrolyte. Electrolyte absorption is needed for ion transport. The microporous membranes usually do not swell on electrolyte absorption.

6.1.2.7. Chemical Stability. The separators should be stable in the battery for a long period of time. They should be inert to both strong reducing and strong oxidizing conditions and should not degrade or loose mechanical strength or produce impurities, which can interfere with the function of the battery. The separator must be able to withstand the strong oxidizing positive electrode and the corrosive nature of the electrolyte at temperatures as high as 75 °C. The greater the oxidation resistance, the longer the separator will survive in a cell. Polyolefins (e.g., polypropylene, polyethylene) exhibit high resistance to most of the conventional chemicals, good mechanical properties, and a moderate temperature range for application making them ideal polymers for lithium-ion battery separators. Polypropylene separators exhibit better oxidation resistance properties when in contact with the positive electrode in a lithium-ion cell. Thus, the oxidation resistance properties of trilayer (PP/PE/PP) separators with PP as the outside layer and PE as inner layer are superior.

6.1.2.7. Dimensional Stability. The separator should lay flat and should not curl at the edges when unrolled, as this can greatly complicate cell assembly. The separator should also not shrink when exposed to electrolyte. The cell winding should not affect the porous structure in any adverse way.

6.1.2.8. Puncture Strength. The separators used in wound cells require a high puncture strength to avoid penetration of electrode material through the separator. If particulate material from the electrodes penetrates the separator, an electrical short will result and the battery will be rejected. The separators used in lithium-ion batteries require more strength then the one used in lithium primary batteries. The primary lithium batteries have only one rough electrode, and thus it requires less strength. As empirically observed, for most applications, the puncture strength should be at least 300 g/mil for separators used in lithium-ion cells. Mix penetration strength is a better measure of separator strength in a battery compared to puncture strength.

6.1.2.9. Mix Penetration Strength. The susceptibility of separators to particle penetration is characterized by mix penetration strength.[49] During the winding of the spiral wrap construction considerable mechanical pressure is applied to the cathode−separator−anode interface. Any loose particle could be forced through the separator and short the cell. The mix penetration strength should be at least 100 kgf/mil for separators used in lithium-ion cells.

6.1.2.10. Thermal Stability. Lithium-ion batteries can be poisoned by water, and so materials going into the cell are typically dried at 80 °C under vacuum. Under these conditions, the separator must not shrink significantly and definitely must not wrinkle. Each battery manufacturer has specific drying procedures. The requirement of less than 5% shrinkage after 60 min at 90 °C (in a vacuum) in both MD and TD direction is a reasonable generalization.

6.1.2.11. Pore Size. A key requirement of separators for lithium batteries is that their pores be small enough to prevent dendritic lithium penetration through them. Membranes with submicrometer pore sizes have proven adequate for lithium batteries.

6.1.2.12. Tensile Strength. The separator is wound with the electrodes under tension. The separator must not elongate significantly under tension in order to avoid contraction of the width. A tensile strength specification is sometimes given, but the key parameter is Young's modulus in the machine direction. Since Young's modulus is difficult to measure, a 2% offset yield is a good measure; less than 2% offset at 1000 psi is acceptable for most winding machines.

6.1.2.13. Skew. Ideally, when a strip of separator is laid out, the separator should be straight and not bow or skew. In practice, however, some skew is often observed. If sufficiently extreme, the skew can cause misalignment between the electrodes and separator. Skew can be measured by laying the separator flat

Table 5. General Requirements for Lithium-ion Battery Separator[90]

parameter	goal
thickness[a,b] (μm)	<25
electrical resistance (MacMullin no.,[c] dimensionless)	<8
electrical resistance (ohms cm^2)	<2
gurley[d] (s)	~ 25/mil
pore size[e] (μm)	< 1
porosity (%)	~ 40
puncture strength[f] (g/mil)	>300
mix penetration strength (kgf/mil)	>100
shrinkage[g] (%)	<5% in both MD and TD
tensile strength[h] (%)	<2% offset at 1000 psi
shutdown temp (°C)	~130
high-temp melt integrity (°C)	>150
wettability	complete wet out in typical battery electrolytes
chemical stability	stable in battery for long period of time
dimensional stability	separator should lay flat; be stable in electrolyte
skew (mm/m)	<0.2

[a] ASTM D5947-96. Standard Test Methods for Physical Dimensions of Solid Plastics Specimens. ASTM International. [b] ASTM D2103. Standard Specification for Polyethylene Film and Sheeting", ASTM International. [c] Caldwell, D. L.; Poush, K. A. U.S. Patent, 4,464,238, 1984. [d] ASTM D726. Standard Test Methods for Identification of Fibers in Textiles. ASTM International. [e] ASTM E128-99. Standard test method for Maximum Pore Diameter and Permeability of Rigid Porous Filters for Laboratory Use. ASTM International. [f] ASTM D3763. Standard Test Method for High-Speed Puncture Properties of Plastics using Load and Displacement Sensors. ASTM International. [g] ASTM D1204. Standard Test methods for Linear Dimensional Changes of Nonrigid Thermoplastic Sheeting or Film at Elevated Temperatures. ASTM International. [h] ASTM D882. Standard Test Method for Tensile Properties of Thin Plastic Sheeting. ASTM International.

on a table parallel with a straight meter stick. The skew should be less than 0.2 mm/m of separator.

6.1.2.14. Shutdown. Lithium-ion batteries separators provide some margin of protection against short circuit and overcharge in lithium-ion cells. The separators exhibit a large increase in impedance at temperature about 130 °C that effectively stops ionic transport between the electrodes.[91,92] The greater the mechanical integrity of the separator above 130 °C, the greater the margin of safety the separator can provide. If the separator loses mechanical integrity, then the electrodes can come into direct contact, react chemically, and result in thermal runaway. The shutdown behavior of a separator can be characterized by heating the separator (saturated with electrolyte) to high temperatures and simultaneously monitoring the electrical resistance of the separator.[92,108]

6.1.2.15. High-Temperature Stability. A separator might provide an extra margin of safety if it can prevent the electrodes from contacting one another at high temperatures. Separators with good mechanical integrity at high temperatures can provide a greater margin of safety for lithium-ion cells. Thermal mechanical analysis (TMA) can be used to characterize the high-temperature stability of separators. Utilizing TMA, the separator is held under constant load and the degree of elongation vs. temperature is measured; at the temperature where the separator loses mechanical integrity, the elongation increases dramatically.

6.1.2.16. Electrode Interface. The separator should form a good interface with the electrodes to provide sufficient electrolyte flow.

In addition to the above properties, the separator must be essentially free of any type of defects (pinholes, gels, wrinkles, contaminants, etc.). All of the above properties have to be optimized before a membrane qualifies as a separator for a lithium-ion battery. The general requirements for lithium-ion battery separators are also summarized in Table 5.

6.1.3. Separator Properties/Characterization

Separators are characterized by structural and functional properties; the former describes what they are and the latter how they perform. The structural properties include chemical (molecular) and microcrystalline nature, thickness, pore size, pore size distribution, porosity, and various chemical and physical properties such as chemical stability, and electrolyte uptake. The functional properties of interest are electrical resistivity, permeability, and transport number. It is useful to characterize separator materials in terms of their structural and functional properties and to establish a correlation of these properties with their performance in batteries. A variety of techniques are used to evaluate separators. Some of these techniques are discussed in this section.

6.1.3.1. Gurley. Separator permeability is usually characterized by air permeability. The gurley number expresses the time required for a specific amount of air to pass through a specific area of separator under a specific pressure. The standard test method is described in ASTM-D726 (B).

The gurley number is used to characterize separators because the measurement is accurate and easy to make, and deviations from specific values are a good indication of problems. Air permeability (gurley) is proportional to electrical resistance (ER), for a given separator morphology.[98] Gurley can be used in place of ER measurements once the relationship between gurley and ER is established. A lower gurley value means higher porosity, lower tortuosity, and accordingly lower ER.

6.1.3.2. Electrical Resistance. The measurement of separator resistance is very important to the art of battery manufacture because of the influence the separator has on electrical performance. Electrical resistance is a more comprehensive measure of permeability then the gurley number, in that the measurement is carried out in the actual electrolyte solution. The ionic resistivity of the porous membrane is essentially the resistivity of the electrolyte that is embedded in the pores of the separator. Typically, a microporous separator, immersed in an electrolyte has an electrical resistivity about 6−7 times that of a comparable volume of electrolyte, which it displaces. It is a function of the membrane's porosity and tortuosity, the resistivity of the electrolyte, the thickness of the membrane, and the extent to which the electrolyte wets the pores of the membrane.[93] The electrical resistance of the separator is the true performance indicator of the cell. It describes a predictable voltage loss within the cell during discharge and allows one to estimate rate limitations.

Classical techniques for measuring electrical resistivity of microporous separators have been described by Falk and Salkind[5] and by Robinson and Walker.[94] The resistivity of an electrolyte is more accurately determined by ac methods since dc can polarize the electrodes and cause electrolysis of the solution. Modern ac impedance measuring systems allow rapid measurements of cell resistance over a wide range or frequencies from which resistance can be calculated free of capacitance effects. Compared to the dc techniques, the equipment required and the theory necessary to interpret the ac techniques are more complex; however, ac measurements yield information about long-range migration of ions and polarization phenomena occurring within the cell. In an ac measurement, a sinusoidal voltage is applied to a cell, and the sinusoidal current passing through the cell as a result of this perturbation is determined. A four-electrode cell is usually used for resistivity measurements. The outer two electrodes serve to apply a sinusoidal potential, and the resulting current passing through the inner two electrodes is measured. This technique is employed to avoid the complications arising from a nonuniform potential field near the outer two electrodes. An excellent review of experimental techniques for measuring electrical resistivity in aqueous solution is available.[95,96]

The separator resistance is usually characterized by cutting small pieces of separators from the finished material and then placing them between two blocking electrodes. The separators are completely saturated with the electrolyte. The resistance (Ω) of the separator is measured at a certain frequency by ac impedance techniques. The frequency is chosen so that the separator impedance is equal to the separator resistance. To reduce the measurement error, it is best to do multiple measurements by adding extra layers. The average resistance of single layer is determined from multiple measurements. The specific resistivity, ρ_s (Ω cm), of the separator saturated with electrolyte is given by

$$\rho_s = \frac{R_s A}{l} \tag{1}$$

where R_s is the measured resistance of separator in Ω, A is the electrode area in cm^2, and l is the thickness of membrane in cm. Similarly, the specific resistivity of the electrolyte, ρ_e (Ω cm), is given by

$$\rho_e = \frac{R_e A}{l} \tag{2}$$

where R_e is the measured resistance of electrolyte in Ω. The ratio of the resistivity of a separator membrane to that of the electrolyte is called the MacMullin number, N_m, which can be used to predict the influence of the separator on battery performance.[97]

$$N_m = \frac{\rho_s}{\rho_e} = \frac{\tau^2}{\epsilon} \tag{3}$$

where τ is the tortuosity and ϵ is the porosity of the separator. The MacMullin number describes the relative contribution of a separator to cell resistance. It is almost independent of electrolyte used and also factors out the thickness of the material. It assumes that the separator wets completely in the electrolyte used for the test. From eqs 1 and 3, the electrical resistance of a microporous membrane is given by the following[5,114]

$$R_m = \rho_e\left(\frac{\tau^2 l}{\epsilon A}\right) \tag{4}$$

It has been shown for Celgard membranes that the membrane resistance can be related to the gurley number by[98]

$$R_m A = \frac{\rho_e}{5 \times 18 \times 10^{-3}} t_{gur} d \tag{5}$$

where R_m is the membrane resistance (Ω), A is the membrane area (cm^2), ρ_e is the specific electrolyte resistance (Ω cm), t_{gur} is the gurley number (10 cm^3 air, 2.3 mmHg), d is the pore size, and $5 \times 18 \times 10^{-3}$ is a scaling factor.

The usual procedure for characterizing battery separators is to cut several test samples from the finished material. Thus, only a small portion of the separator is actually examined. Ionov et al. has proposed an alternative technique to measure the resistance of a separator over a large separator area.[99] In this technique, the separator material is passed through an electrolyte bath between electrical resistance measuring transducers. The set of transducers installed in the bath transverse to the moving sheet of separator material examines the whole surface of the material. If the production process ensures good uniformity in the physicochemical properties of the separator material over the whole surface, the transducer outputs will clearly be close to one another. A nonuniform separator will cause significant deviations from the average value at various sections of the material. In this case, the sections having lower or higher resistance compared with the average value should be regarded as flawed.

6.1.3.3. Porosity. The porosity is important for high permeability and also for providing a reservoir of electrolyte in the cell. Higher and uniform porosity is desirable for unhindered ionic current flow. Nonuniform porosity leads to nonuniform current density and can further lead to reduced activity of the electrodes. Cell failure can result because during discharge some areas of the electrodes work harder then other.

Porosity of a separator is defined as the ratio of void volume to apparent geometric volume. It is usually calculated (eq 6) from the skeletal density, basis weight, and dimensions of the material and so may not reflect the accessible porosity of the material.

$$\text{porosity (\%)} = \left[1 - \frac{(\text{sample weight}/\text{sample volume})}{\text{polymer density}}\right] \times 100 \quad (6)$$

The standard test method is described in ASTM D-2873. The actual or accessible porosity can also be determined by the weight of liquid (e.g., hexadecane) absorbed in the pores of the separator. In this method, the separator weight is measured before and after dipping in hexadecane solvent, and the porosity is calculated (eq 7) by assuming that volume occupied by hexadecane is equal to the porous volume of the separator.

$$\text{porosity (\%)} = \frac{\text{volume occupied by hexadecane}}{(\text{volume of polymer} + \text{volume occupied by hexadecane})} \times 100 \quad (7)$$

6.1.3.4. Tortuosity. Tortuosity is the ratio of mean effective capillary length to separator thickness. The tortuosity factor, τ of a separator can be expressed by

$$\tau = \frac{l_s}{d} \quad (8)$$

where l_s is the ion path through the separator and d is the thickness of the separating layer.

Tortuosity is a long-range property of a porous medium, which qualitatively describes the average pore conductivity of the solid. It is usual to define τ by electrical conductivity measurements. With knowledge of the specific resistance of the electrolyte and from a measurement of the sample membrane resistance, thickness, area, and porosity, the membrane tortuosity can be calculated from eq 3.

This parameter is widely used to describe the ionic transport by providing information on the effect of pore blockage. A tortuosity factor $\tau = 1$, therefore, describes an ideal porous body with cylindrical and parallel pores, whereas values of $\tau > 1$ refer to more hindered systems. Higher tortuosity is good for dendrite resistance but can lead to higher separator resistance.

6.1.3.5. Pore Size and Pore Size Distribution. For any battery applications, the separator should have uniform pore distribution to avoid performance losses arising from nonuniform current densities. The submicrometer pore dimensions are critical for preventing internal shorts between the anode and the cathode of the lithium-ion cell, particularly since these separators tend to be as thin as 25 μm or less. This feature will be increasingly important as battery manufacturers continue to increase the cell capacity with thinner separators. The pore structure is usually influenced by polymer composition, and stretching conditions, such as drawing temperature, drawing speed, and draw ratio. In the wet process, the separators produced by the process of drawing after extraction (as claimed by Asahi Chemical and Mitsui Chemical) are found to have much larger pore size (0.24−0.34 μm) and wider pore size distribution than those produced by the process of extraction (0.1−0.13 μm) after drawing (as claimed by Tonen).[58]

The testing of battery separators and control of their pore characteristics are important requirements for proper functioning of batteries. Mercury porosimetry has been historically used to characterize the separators in terms of percentage porosity, mean pore size and pore size distribution.[100] In this method, the size and volume of pores in a material are measured by determining the quantity of mercury, which can be forced into the pores at increasing pressure. Mercury does not wet most materials, and a force must be applied to overcome the surface tension forces opposing entry into the pores.

The hydrophobic (e.g. polyolefins) separators are also characterized with Aquapore (non-mercury porosimetry) technique, where water is used in place of mercury. This is a very useful technique for characterizing polyolefin-based separators used in lithium batteries.[101] Porosimetry gives pore volume, surface area, mean pore diameter, and pore size distribution. In a typical experiment, the sample is placed in the instrument and evacuated. As the pressure increase, the quantity of water forced into the pores increases in proportion to the differential pore volume, the size of the pores corresponding to the instantaneous pressure. Thus, increasing the pressure on a membrane having a given pore size distribution results in a unique volume vs pressure or pore diameter curve. The pressure required for intrusion of water in to a pore of diameter, D, is given by following equation

$$D = \frac{4\gamma \cos \theta}{p} \quad (9)$$

where D is the diameter of the pore assuming the pore to be cylindrical, p is the differential pressure, γ is the surface tension of the nonwetting liquid, water, and θ is the contact angle of water. The pores generally are not of spherical shape of a constant diameter. They usually vary in their form and size. Thus, statements of any pore diameter are always to be viewed with the above in mind.

Another technique, capillary flow porometry has been developed by Porous Materials Inc.[102] to characterize battery separators.[103,104] The instrument can measure a number of characteristics of battery separators such as size of the pore at its most constricted part, the largest pore size, pore size distribution, permeability, and envelope surface area.[109]

Scanning electron microscopy (SEM) is also used to examine separator morphology. SEM pictures of some commercial membranes are shown in Figures

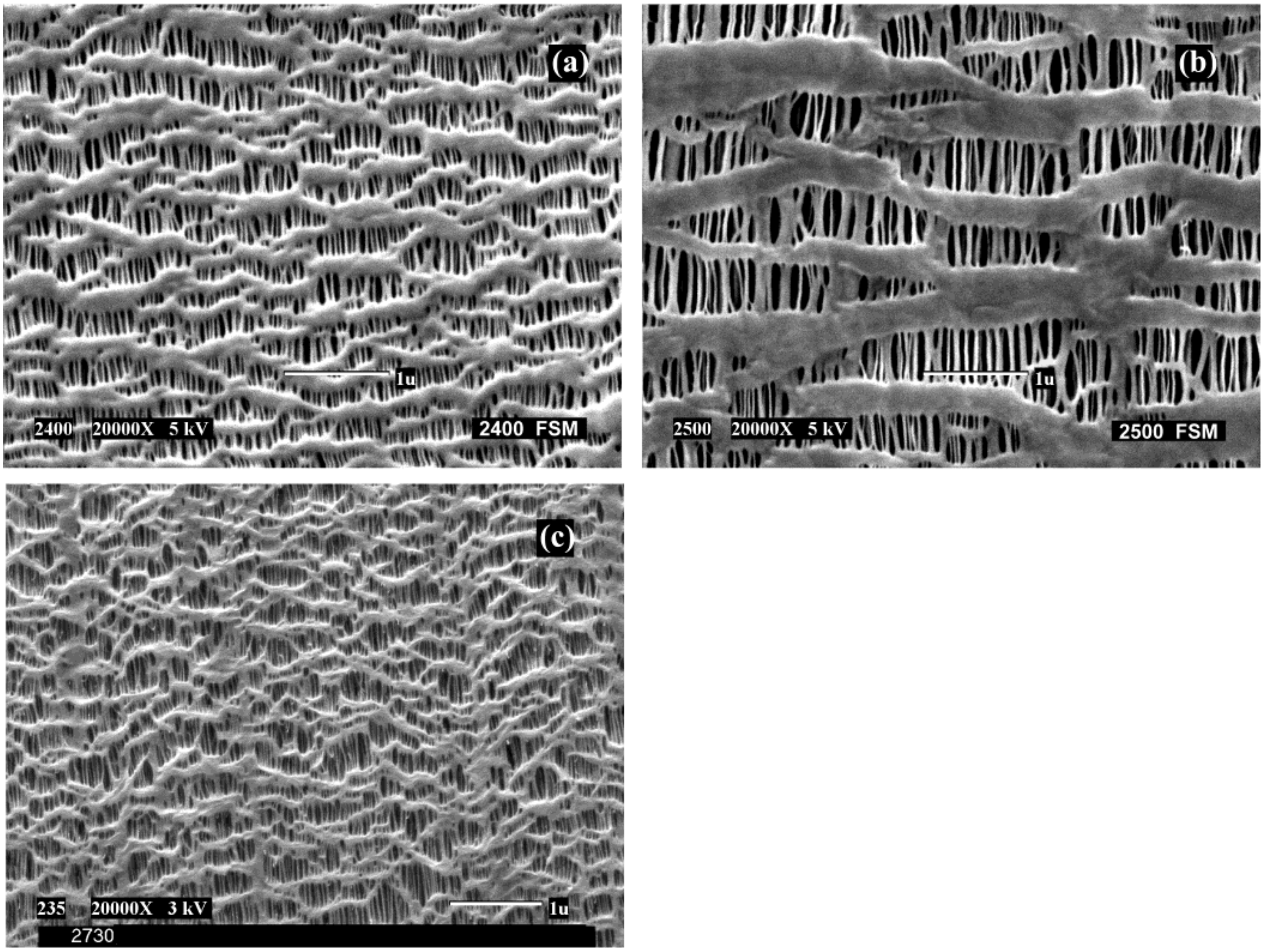

Figure 4. Scanning electron micrographs of the surface of single layer Celgard separators used in lithium batteries: (a) 2400 (PP), (b) 2500 (PP), and (c) 2730 (PE).

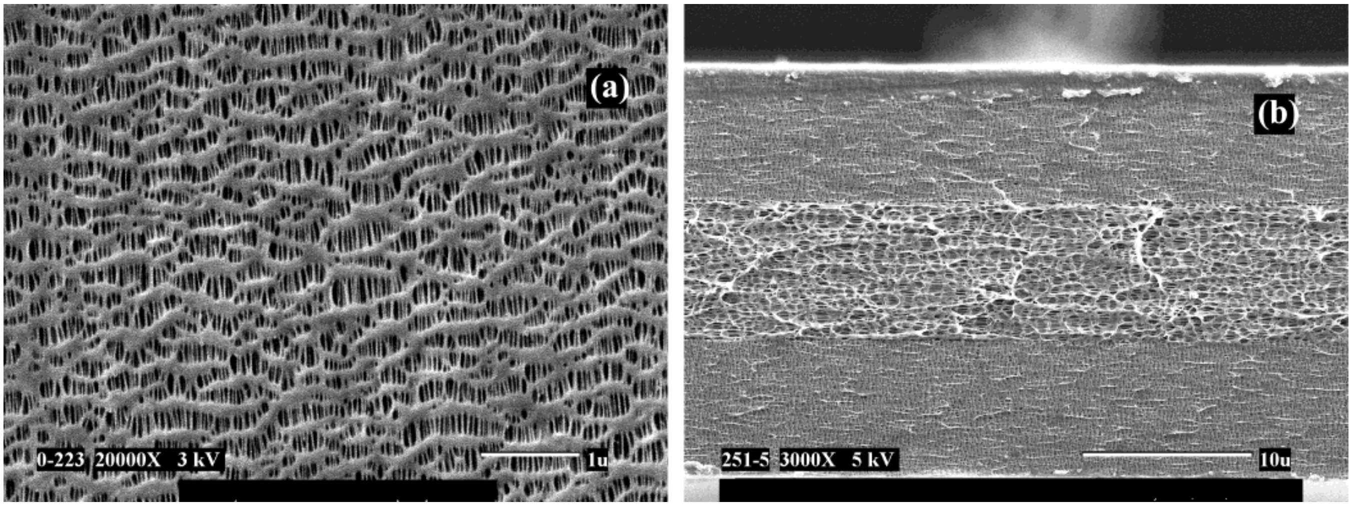

Figure 5. Scanning electron micrographs of Celgard 2325 (PP/PE/PP) separator used in lithium-ion batteries: (a) surface SEM and (b) cross-section SEM.

4−6. The surface SEM of Celgard 2400, 2500, and 2730 are shown in Figure 4. It is clear from the images that the pores are uniformly distributed. Both Celgard 2400 and 2500 are single layer PP separators, but the pore size of Celgard 2500 is substantially larger than Celgard 2400. Thus, it has lower resistance and is more suited for high rate applications. Figure 5 shows the surface SEM and cross-section SEM of Celgard 2325. The surface SEM only shows the PP pores while the PE pores are visible in the cross-section. It is clear from the image that all three layers are of equal thickness. The SEM of separators made by wet process are shown in Figure 6. The pore structure of all of these membranes is very similar.

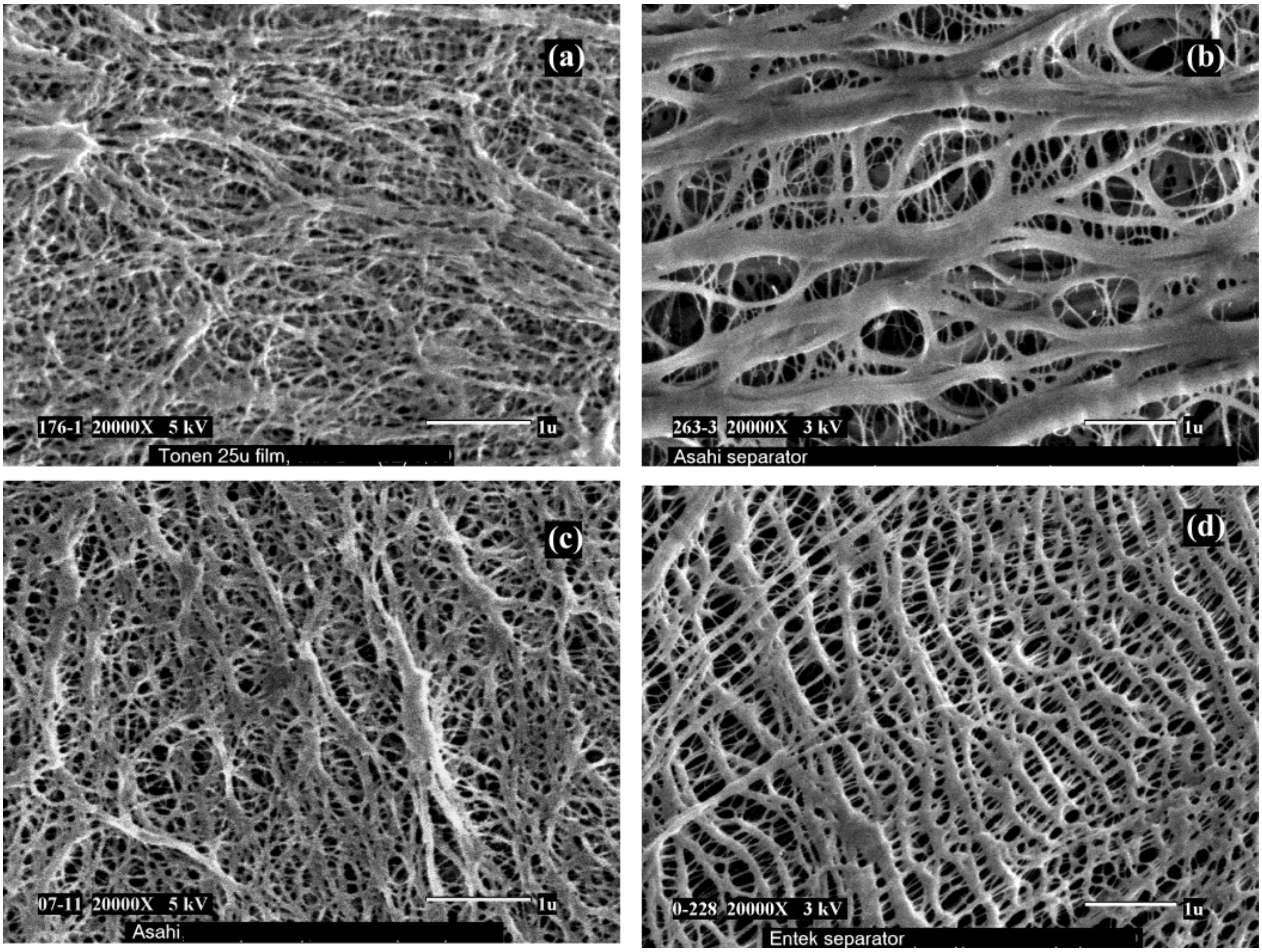

Figure 6. Scanning electron micrographs of separators made by wet process and used in lithium-ion batteries: (a) Setela (Tonen), (b) Hipore-1 (Asahi), (c) Hipore-2 (Asahi), and (d) Teklon (Entek).

Asahi-1 (Figure 6b) separator has significantly larger pores compared to the other membranes.

Image analysis has been used to characterize the pore structure of synthetic membrane materials.[105] The Celgard films have also been characterized by scanning tunneling microscopy, atomic force microscopy, and field emission scanning electron microscopy.[53,106] The pore size of the Celgard membranes can also be calculated from eq 5, once the MacMullin number and gurley values are known.

6.1.3.6. Puncture Strength. A separator is required to have sufficient physical strength to endure the rigors of cell assembly and day-to-day charge−discharge cycling. Physical strength is required to withstand basic handling, cell blocking/assembly, physical shock, punctures, abrasion, and compression.

The puncture strength (PS) is the weight that must be applied to a needle to force it completely through a separator.[45,107] It has been used to indicate the tendency of separators to allow short-circuits in a cell that may occur due to holes generated in the separator by the rough surface of an electrode during the battery assembly and charge−discharge cycle. The PS requirement for lithium-ion batteries is higher them lithium-foil batteries, because the separator must contend with two rough surfaces. Commercially available puncture strength machines made for textiles tend to give meaningless results when testing battery separator membranes. More reproducible results can be obtained with a load frame (such as an Instron Machine). The mix penetration strength is a better measure of mechanical strength for battery separators as it measures the force required to create a short through the separator when electrode mix is pushed through it.

The strength of the separator depends greatly on the materials used and the manufacturing method. The wet-biaxial method simultaneously stretches in the MD and TD directions and thus achieves a material that has tensile modulus and rupture strength in both directions. Both high polymer entanglement and stretching help increase the physical strength of the separator.

6.1.3.7. Mix Penetration Strength. The force required to create a short through a separator due to mix (electrode material) penetration defines mix penetration strength. In this test force (with a $^{1}/_{2}$ in. diameter ball) is applied on the positive electrode/separator/negative electrode sandwich, and the force at which the mix penetrates through the separator and creates an electronic short is called mix penetration force. Mix penetration strength is used to indicate the tendency of separators to allow short-

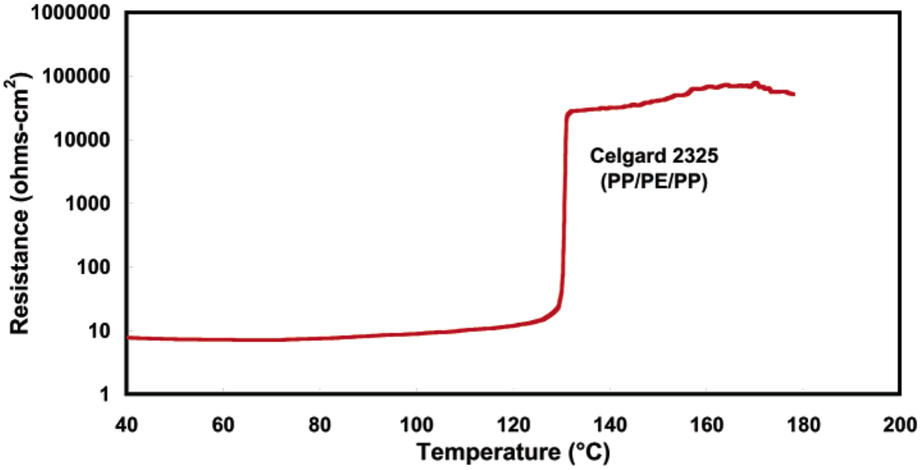

Figure 7. Internal impedance (at 1 kHz) of Celgard 2325 (PP/PE/PP) separator as a function of temperature. Heating rate: 60 °C/min.

circuits during battery assembly. The mix penetration resistance test is more closely related to particle penetration resistance compared to puncture resistance.[49]

6.1.3.8. Tensile Strength. The tensile strength measurements (e.g., Young's modulus, percent offset strength, elongation at break, and stress at break) can be made by utilizing widely known standard procedures. These tests are carried out in both MD and TD directions. The tensile properties are dependent on the manufacturing process. The uniaxially oriented films have high strength in only one direction, whereas biaxially oriented films are more uniformly strong in both MD and TD directions. ASTM test method D88-00, "Standard test method for tensile properties of thin plastic sheeting", is an appropriate test.

The separator should be strong enough to withstand mechanical handling during cell winding and assembly. It should be dimensionally stable and should not neck down during winding. The decrease in width will allow the electrodes to touch each other and create a short. Thus, the tensile property of the separator should be very strong in MD direction compared to TD direction.

6.1.3.9. Shrinkage. Shrinkage test is carried out on both MD and TD directions. In this test, the dimensions of separators are measured and then stored at 90 °C for a fixed time. The shrinkage is then calculated from the change in dimensions as shown in eq 10.

$$\text{shrinkage (\%)} = \frac{L_i - L_f}{L_i} \times 100 \qquad (10)$$

where L_i is the initial length and L_f is the final length of separator after high temperature storage. The uniaxially stretched separators tend to shrink in the MD direction only, while the biaxially stretched separators shrink in both MD and TD directions. The shrinkage of separators can also be compared by carrying out the thermal mechanical analysis (TMA) test at a constant load and rate.

6.1.3.10. Shutdown. Separator shutdown is a useful and essential mechanism for limiting temperature and preventing venting in short-circuited cells.[108] It usually takes place close to the melting temperature of the polymer when the pores collapse turning the porous ionically conductive polymer film into a nonporous insulating layer between the electrodes. At this temperature there is a significant increase in cell impedance and passage of current through the cell is restricted. This prevents further electrochemical activity in the cell, thereby shutting the cell down before an explosion can occur.

The ability of the PE based separator to shutdown the battery is determined by its molecular weight, percent crystallinity (density) and process history. Material properties and processing methods might need to be tailored so that the shutdown response is spontaneous and complete. The optimization needs to be done without affecting the mechanical properties of the material in the temperature range of interest. This is easier to do with the trilayer separators manufactured by Celgard since one material is utilized for the shutdown response and another for the mechanical properties. Polyethylene containing separators, in particular trilayer laminates of polypropylene, polyethylene, and polypropylene, appear to have the most attractive properties for preventing thermal runaway in lithium-ion cells.[109,110] The shutdown temperature of 130 °C is usually enough to control the cell heating and avoid thermal runaway in lithium-ion cells. A lower temperature shutdown will be desirable if it does not affect the separator mechanical properties or high-temperature cell performance in any adverse way.

The shutdown property of separators is measured by measuring the impedance of a separator while the temperature is linearly increased.[92,108] Figure 7 shows the actual measurement for Celgard 2325 membrane. The heating rate was around 60 °C/min, and the impedance was measured at 1 kHz. The rise in impedance corresponds to a collapse in pore structure due to melting of the separator. A 1000-fold increase in impedance is necessary for the separator to stop thermal runaway in the battery. The drop in impedance corresponds to opening of the separator due to coalescence of the polymer and/or to penetration of the separator by the electrodes; this phenomenon is

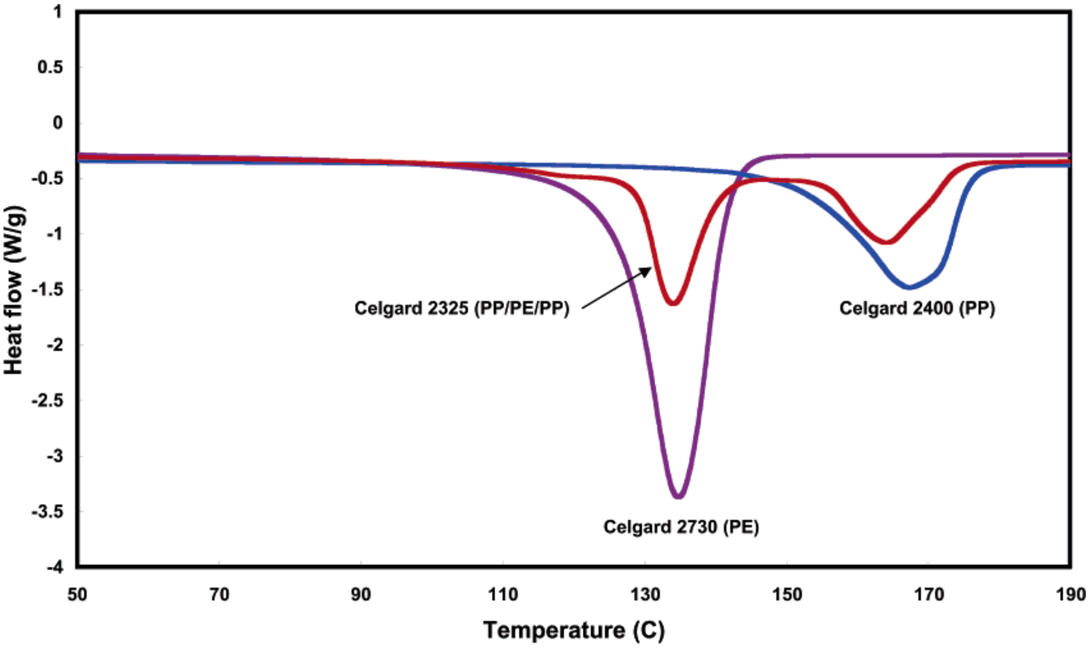

Figure 8. DSC of Celgard 2730 (PE), 2400 (PP), and 2325 (PP/PE/PP).

referred to as a loss in "melt integrity". This test is fairly reliable in indicating the temperature at which the impedance rises but shows some variability in characterizing the subsequent drop in impedance.

In Figure 7, the shutdown behavior of a multilayer (PP/PE/PP) separator (Celgard 2325) is shown. The impedance rise occurred near the melting point of polyethylene (130 °C) and remained high until such time as the melting point of polypropylene (165 °C) is attained. The shutdown temperature of the separator is governed by the melting point of the separator material. At the melting point the pores in the separator collapse to the form a relatively nonporous film between the anode and the cathode. This was confirmed by DSC as shown in Figure 8. The DSC scan in Figure 8 gives a peak melting temperature of 135 °C for Celgard 2730, 168 °C for Celgard 2400, and 135/165 °C for Celgard 2325. The shutdown behavior of thinner separators (<20 μm) is very similar to thicker separators. The battery manufacturers have been very successful in using the thinner separators without compromising on the shutdown behavior of the separators.

Laman et al. introduced the use of impedance measurements as a function of temperature to characterize shutdown separators.[92] Using a temperature scan rate of 1 °C/min, they found that the impedance increased several orders of magnitude near the melting point of the separator. They verified the patent claims of Lundquist et al.[111] that bilayer separators of PE and PP gave a temperature window of high impedance extending approximately between the melting point of the polymers. The concept of using separators consisting of distinct layers, one of which could act as a fuse, was developed by Lundquist et al.[112,113] Laman's results have been corroborated by Geiger et al.[40] and Spotnitz et al.[108,114] Spotnitz et al. developed a thin layer cell which allowed temperature scan rates of 5 °C/min and higher and obtained results similar to those of Laman et al.

Prior work related with shutdown separators also involved application of waxes on membranes.[115,116] In these cases, the wax or low melting polymers were coated on the polyolefin separator. The disadvantage of this technique is that the coating can block the pores of the separator and thus can affect the performance by increasing separator resistance. Moreover, the coating level has to be very high to get complete shutdown.

The shutdown characteristic provides protection from external short-circuit and during cell overcharge. It provides little protection from internal shorts should they occur. Should the electrodes touch each other or become shorted from a dendritic growth of soluble impurity or other dendrite forming soluble material, the separator only helps in avoiding delayed failures. In the case of an instant failure during an internal short circuit, the heating rate is too high and the separator shutdown is not fast enough to control the heating rate.

6.1.3.11. Melt Integrity. The separators used in lithium-ion batteries should have high-temperature melt integrity. The separator should maintain its melt integrity after shutdown so that the electrodes do not touch and create a short. This helps in avoiding the thermal runaway even when the cell is exposed to high temperatures. Thermal mechanical analysis (TMA) is a very good technique to measure the high-temperature melt integrity of separators.

TMA involves measuring the shape change of a separator under load while the temperature is linearly increased. Typically, separators show some shrinkage and then start to elongate and finally break as shown in Figure 9. This test utilizes a small separator samples (about 5−10 mm length (MD) and

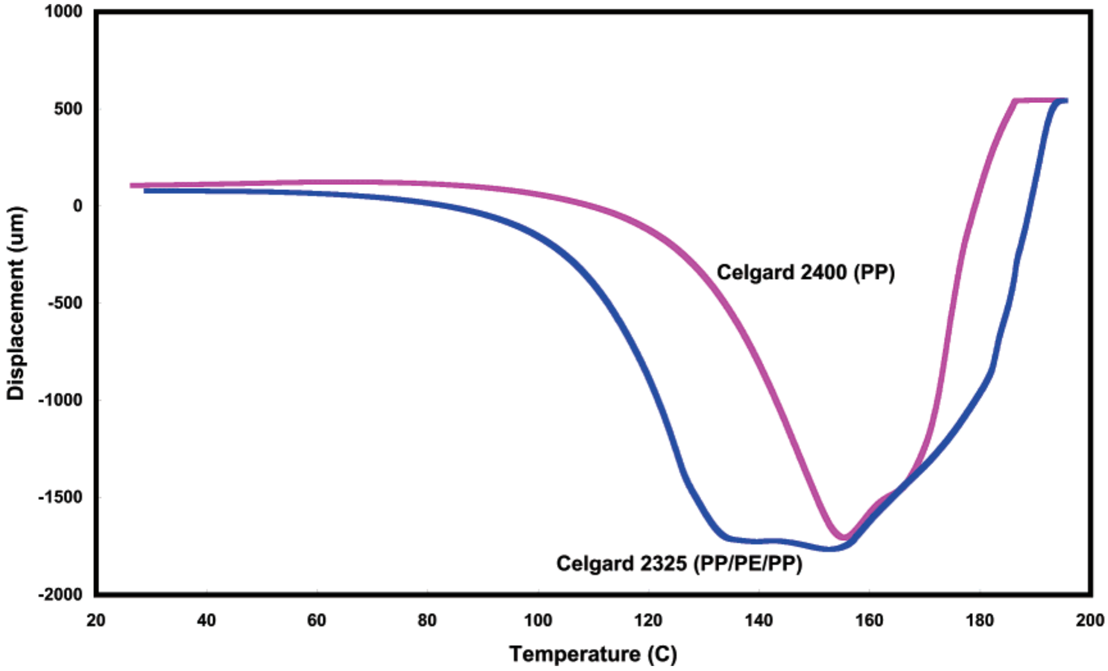

Figure 9. TMA of Celgard 2400 (PP) and 2325 (PP/PE/PP). A constant load (2 g) is applied while the temperature is ramped at 5 °C/min.

Table 6. TMA Data for Typical Celgard Separators

	Celgard 2400	Celgard 2325
shrinkage onset temp (°C)	121	106
deformation temp (°C)	156	135, 154
rupture temp (°C)	183	192

about 5 mm width), which is held in mini-instron type grips. The sample is held with a constant 2 g load while the temperature is ramped at 5 °C/min past the melting point until the tension ruptures the film. Three parameters are reported from TMA test—shrinkage onset temperature, melt temperature, and melt rupture temperature. It has proved to be a more reproducible measure of melt integrity of the separator.[108]

Figure 9 shows the TMA data for two different Celgard membranes. The shrinkage onset temperature, deformation temperature, and rupture temperature are summarized in Table 6. The single layer PP membrane (Celgard 2400) showed a higher softening temperature (~121 °C), a deformation temperature around 160 °C, and a very high rupture temperature around 180 °C. The multilayer polypropylene/polyethylene/polypropylene separator (Celgard 2325) combined the low-temperature shutdown property of polyethylene with the high-temperature melt integrity of polypropylene, resulting in a separator with softening (~105 °C) and melt temperature (~135 °C) very similar to that of PE and rupture temperature (~190 °C) very similar to that of PP.

Separators with melt integrity greater than 150 °C are desirable for lithium-ion cells. The trilayer separators with polypropylene on the outside help in maintaining the melt integrity of the separators at higher temperatures compared to single layer PE separators. This is especially important for bigger lithium-ion cells being developed for hybrid and electric vehicles.

6.1.3.12. Wettability and Wetting Speed. Two physical properties of separators, which are important to the operating characteristics of a battery, are electrolyte absorption and electrolyte retention. Any good separator should be able to absorb a significant amount of electrolyte and also retain the absorbed electrolyte when the cell is in operation. These are more important in sealed cells where no free electrolyte is present. A maximum amount of electrolyte in the separator is desirable to achieve minimum cell internal resistance.

The separator wettability can limit the performance of batteries by increasing the separator and cell resistance. Separator wetting speed can be correlated with electrolyte filling time in real cells. The wetting speed is determined by the type of polymer (surface energy), pore size, porosity, and tortuosity of the separators. There is no generally accepted test for separator wettability. However, simply placing a drop of electrolyte on the separator and observing whether the droplet quickly wicks into the separator is a good indication of wettability. The contact angle is also a good measure of wettability.

The uptake of electrolyte by many hydrophobic polymer separators can be enhanced either by wetting agents or ionic-functional groups (e.g. ion-exchange membranes).

6.1.4. Effect of Separator on Cell Performance and Safety

Although the material of a battery separator is inert and does not influence electrical energy storage or output, its physical properties greatly influence the performance and safety of the battery. This is especially true for lithium-ion cells, and thus the battery manufacturers have started paying more attention to separators while designing the cells. The cells are designed in such a way that separators do not limit the performance, but if the separator properties are

Table 7. Safety and Performance Tests for Lithium-Ion Batteries and the Corresponding Important Separator Property and Its Effect on the Cell Performance and/or Safety

cell property	separator property	comments
cell capacity	thickness	cell capacity can be increased by making the separator thinner
cell internal resistance	resistance	separator resistance is a function of thickness, pore size, porosity, and tortuosity
high rate performance	resistance	separator resistance is a function of thickness, pore size, porosity, and tortuosity
fast charging	resistance	low separator resistance will aid in overall faster charging by allowing higher and/or longer constant current charging
high-temp storage	oxidation resistance	oxidation of separators can lead to poor storage performance and reduce performance life
high-temp cycling	oxidation resistance	oxidation of separators can lead to poor cycling performance
self-discharge	weak areas, pinholes	soft shorts during cell formation and testing can lead to internal current leakage
long-term cycling	resistance, shrinkage, pore size	high resistance, high shrinkage and very small pore size can lead to poor cycling performance
overcharge	shutdown behavior; high-temp melt integrity	separator should completely shutdown and then maintain its melt integrity at high temp
external short circuit	shutdown behavior	separator shutdown stops the cells from overheating
hotbox	high-temp melt integrity	separator should be able to keep the two electrodes apart at high temp
nail crush	shutdown (to stop delayed failure)	in the case of internal shorts, the separator may be the only safety device to stop the cell from overheating
bar crush	shutdown (to stop delayed failure)	in the case of internal shorts, the separator may be the only safety device to stop the cell from overheating

not uniform, or if there are other issues, it can affect the performance and safety of cells. This section will focus on the effect of the separator properties on cell performance and safety. Table 7 shows different types of safety and performance tests for lithium-ion batteries and the corresponding important separator property and how it affects performance and/or safety.

To achieve good performance of lithium-ion cells, the separators should have low resistance, low shrinkage and uniform pore structure. The separator with high resistance will perform poorly during high rate discharge and will also increase the cell charging time. Low shrinkage is a very important characteristic for separators, especially for higher capacity cells. These cells are used in high-speed laptop computers, which can experience higher temperatures (~70−75 °C) under certain conditions.[117] This can lead to shrinkage of separators and ultimately higher cell resistance and poor long-term cycling. The shrinkage in TD direction can lead to safety issues because of an internal short between the electrodes. Larger pores can lead to shorts during cell manufacturing or can fail during hipot testing. Larger pores will allow more soft shorts and higher self-discharge, especially during high-temperature storage. Very small pore size can lead to higher resistance and poor cycle life during high-temperature cycling and storage. Thus, the pore size of the separator should be optimized to achieve good strength and performance.

One of the ways to increase cell capacity is by decreasing the thickness of separators. The newer high capacity cells (>2.0 A h) generally use 20 and 16 μm separators as compared to 25 μm separators used in cells with 1.6−1.8 A h capacity. The thinner separators offer lower resistance and help in increasing the capacity. However, they can hold less electrolyte and their mechanical strength is not as high as thicker separators. Thus, appropriate changes should be made in cell design to keep the cell safe. The handling and manufacturing of thinner separators is also a challenge for the separator manufacturers. They are required to maintain the same electrical and mechanical properties and to have better quality for thinner separators. The separator manufacturers have installed better controls and quality standards and have started offering 16-μm separators. A lot of battery experts are of the opinion that the 16-μm is the thinnest they can use and still maintain the stringent performance and safety requirements of lithium-ion cells.

The separators inside the lithium-ion batteries experience extreme oxidizing environment on the side facing the positive electrode and extreme reducing environment on the side facing the negative electrode. The separators should be stable in these conditions during long-term cycling especially at high temperatures. Separators with poor oxidation resistance can lead to poor high-temperature storage performance and poor long-term cycling behavior. The oxidation resistance properties of trilayer (PP/PE/PP) separators with PP as the outside layer and PE as inner layer is superior compared to polyethylene separators. This is because of the better oxidation resistance properties of polypropylene in contact with the positive electrode in a lithium-ion cell.

The products formed by the decomposition of the electrolyte can also block the pores of the separator, leading to increase in cell resistance. The separators with lower resistance also helps in better low temperature performance. At very low temperatures, the resistance of the electrolytes is very high and thus smaller contribution from separator helps in keeping the cell resistance lower.

Zeng et al.[118] has shown that small amounts of active lithium metal could be added to a lithium-ion battery via the separator by using vacuum deposition techniques. The lithium films (4−8 μm) were deposited onto a microporous PP film and showed that the lithium electrochemically reacted with either electrode and thus the intrinsic irrereversible capacity of the negative electrode was compensated for using volumetrically efficient lithium metal. This may be a novel idea to allow higher capacity designs but is likely impractical and uneconomical due to issues involved with lithium plating on polymer films and handling the resulting films.

The lithium-ion cells have demonstrated power loss when aged and/or cycled at high temperatures. Norin et al.[119] demonstrated that the separator is at least partly responsible for the power loss due to the intrinsic increase in its ionic resistance. They showed that impedance increased significantly upon cycling and/or aging of lithium-ion cells at elevated temperatures and that separators accounts for ∼15% of the total cell impedance rise. They later reported that the loss in ionic conductivity of the separator was due to blocking of the separator pores with the products formed due to electrolyte decomposition, which was significantly accelerated at elevated temperatures.[120]

The U.S. Department of Transportation (DOT) classifies all lithium-ion batteries as hazardous materials for shipping in the same category as lithium metal primary batteries.[121] It grants exceptions based on the cell capacity and ability of the cells to pass specified tests. There are several groups that regulate, or provide testing, to verify safe operation of lithium-ion cells under abuse conditions. In addition, the UL Laboratories,[122,123] the International Electrotechnic Commission,[124] and the United Nations[125] have developed standardized safety testing procedures. These tests are designed to ensure that cells are safe to ship and are resistant to typical abuse conditions such as internal shorting, overcharge, overdischarge, vibration, shock, and temperature variations that may be encountered in normal transportation environments.

Underwriters Laboratories (UL) requires that consumer batteries pass a number of safety tests (UL 1642[126] and UL-2054[127]). There are similar recommendations from UN for transport of dangerous goods,[128] and from the International Electrotechnical Commission (IEC) and Japan Battery Association.[129] An abnormal increase in cell temperature can occur from internal heating caused by either electrical abuse—overcharge or short circuit—or mechanical abuse—nail penetration or crush. A higher cell temperature could also be a result of external heating. For this reason, battery packs containing lithium-ion cells are designed with safety control circuits that have redundant safety features (PTC, CID, vent, thermal fuse, etc.). Shutdown separators are one of the safety devices inside the cell and act as a last line of defense. The separator shutdown is irreversible, which is fine for polyethylene-based separators, which melt around 130 °C.

The impedance of the separator increases by 2−3 orders of magnitude due to an increase in cell temperature, which results from cell abuse (e.g., short circuit, overcharge). The separator should not only shutdown around 130 °C, but it should also maintain its mechanical integrity at higher temperatures, preferably at temperatures. If the separator does not shutdown properly then the cell will continue to heat during an overcharge test and can lead to thermal runaway. The high-temperature melt integrity of separators is also a very important property to keep the cell safe during extended overcharge or during extended exposure to higher temperatures.

Figure 10 shows a typical short-circuit curve for an 18650 lithium-ion cell with shutdown separator, $LiCoO_2$ positive electrode, and MCMB carbon negative electrode. The cell does not have other safety devices (e.g., CID, PTC), which usually work before separator shutdown. As soon as the cell is short-circuited externally through a very small shunt resistor, the cell starts heating because of the large current drained through the cell. The shutdown of the separator, which occurs around 130 °C, stops the cell from heating further. The current decrease is caused by increase of battery internal resistance due to separator shutdown. The separator shutdown helps in avoiding the thermal runaway of the cell.

Cells can be overcharged when the cell voltage is incorrectly detected by the charging control system or when the charger breaks down. When this happens, the lithium ions remaining in the cathode are removed and more lithium ions are inserted into the anode then under standard charging conditions. If the lithium insertion ability of the carbon anode is small, lithium metal in the form of dendrites may be deposited on the carbon and this causes a drastic reduction in thermal stability. At higher charging rates, the heat output increases greatly because the joule heat output is proportional to I^2R. Several exothermic reactions (e.g., reaction between lithium and electrolyte, thermal decomposition of anode and cathode, thermal decomposition of electrolyte, etc.) occur inside the cell as its temperature increases. Separator shutdown happens when the cell temperature reaches the melting point of polyethylene as shown in Figure 11. The CID and PTC of the 18650 cells was removed to test the performance of separator alone. The current decrease is caused by increase of battery internal resistance due to separator shutdown. Once the pores of the separator have closed due to softening, the battery cannot continue to be charged or discharged, and thus thermal runaway is prevented. During continued overcharge, the separator should maintain its shutdown feature and should not allow the cell to heat again. It should also maintain its melt integrity and should not allow the two electrodes to touch each other.

The separator should also not allow any dendrite to penetrate through the separator to avoid internal shorts. During an internal short, the separator is the only safety device that can stop the thermal runaway, if the failure is not instant. If the heating rate is too high, then instant failure will occur which cannot be stopped by separator shutdown. If the heating rate

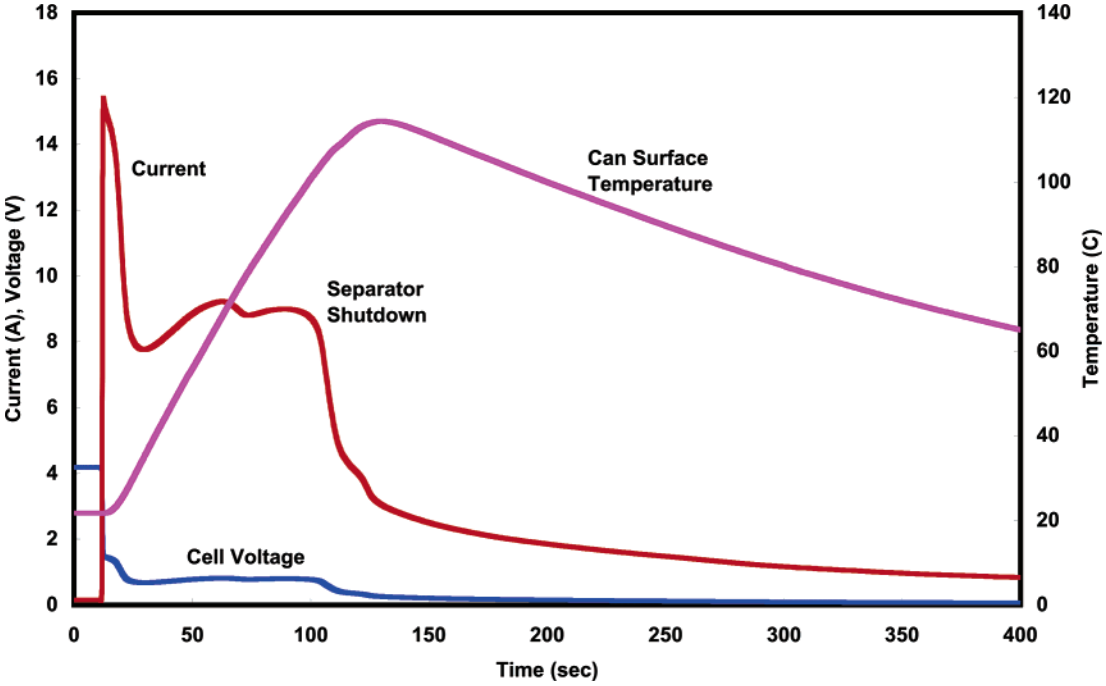

Figure 10. Typical short-circuit behavior of a 18650 lithium-ion cell with shutdown separator and without PTC (positive temperature coefficient) and CID (current interrupt device). This test simulates an external short circuit of a cell.

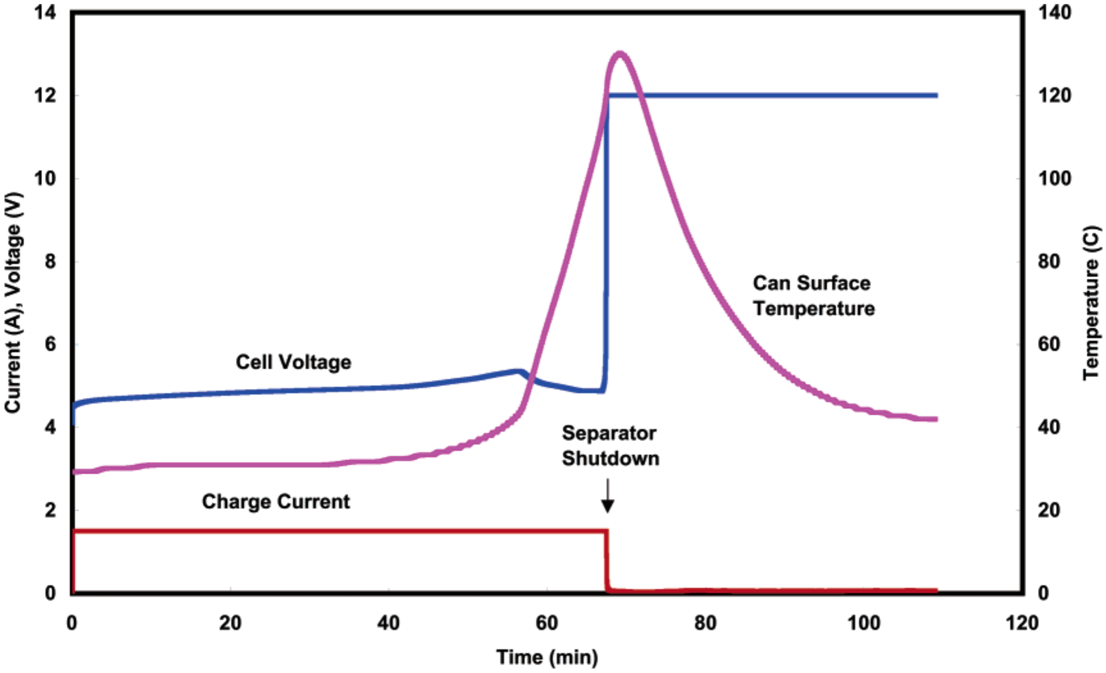

Figure 11. Typical overcharge behavior of a 18650 lithium-ion cell with shutdown separator. The PTC (positive temperature coefficient) and CID (current interrupt device) were removed from the cell header.

is not too high then the separator shutdown can help in controlling the heating rate and stop thermal runaway.

Generally in a nail penetration test, an instantaneous internal short would result the moment the nail is tucked into the battery. Enormous heat is produced from current flow (double layer discharge and electrochemical reactions) in the circuit by the metal nail and electrodes. Contact area varies according to depth of penetration. The shallower the depth, the smaller the contact area and therefore the greater the local current density and heat production. Thermal runaway is likely to take place as local heat generation induces electrolyte and electrode materials to decompose. On the other hand, if the battery is fully penetrated, the increased contact area would lower the current density, and consequently all tests would pass the nail penetration test. Internal short-circuit tests are more difficult to pass then the external short-circuit tests described earlier, because contact area between metal nail contact is smaller than the contact area between current collectors, where the current density would therefore be larger.

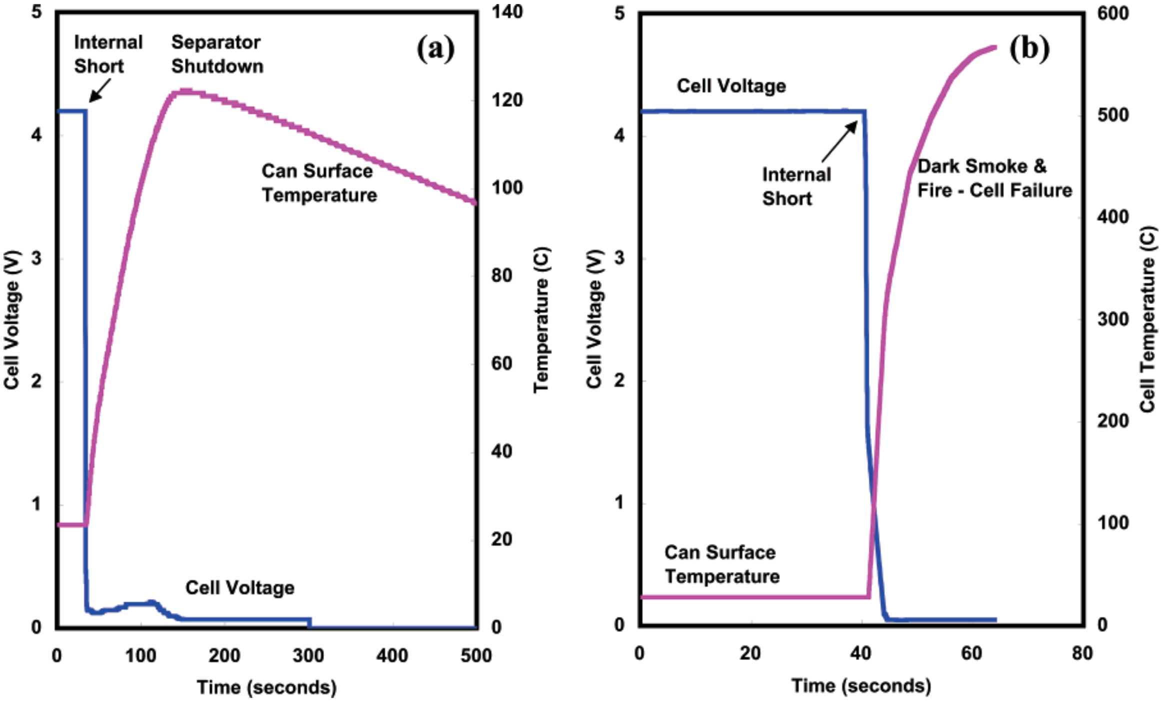

Figure 12. Typical nail penetration behavior of a 18650 lithium-ion cell with shutdown separator. This test simulates internal short circuit of a cell. Key: (a) cell passed nail penetration test; (b) cell failed nail penetration test.

Figure 12 shows the typical nail penetration behavior of a 18650 lithium-ion cell with shutdown separator, $LiCoO_2$ positive electrode, and MCMB carbon negative electrode. Clearly, there was a voltage drop from 4.2 to 0.0 V, instantaneously, as the nail penetrates through (when an internal short circuit occurs), and the temperature rose. When the heating rate is low, the cell stops heating when the temperature is close to separator shutdown temperature as shown in Figure 12a. If the heating rate is very high, then the cell continues to heat and fails the nail penetration test as shown in Figure 12b. In this case, the separator shutdown is not fast enough to stop cell from thermal runaway. Thus, the separator only helps in avoiding delayed failures in the case of internal short circuit as simulated by nail and bar crush tests. Separators with high-temperature melt integrity and good shutdown feature (to avoid delayed failures) are needed to pass the internal short-circuit test. Thinner separators ($<20\ \mu$m) used in high capacity cells should offer shutdown and high-temperature melt integrity properties similar to those of thicker separators. The decrease in separator strength should be balanced with changes in cell design. The separator properties across the length and width should be very uniform to keep the cell safe during abnormal use.

The mechanism and characteristics of thermal cutoff devices in several prismatic lithium-ion cells was studied by Venugopal[130] by monitoring the impedance at 1 kHz and the open circuit voltage (OCV) of the cells as a function of temperature. All the cells studied contained PE-based separators with a shutdown temperature between 130 and 135 °C. Within this narrow temperature range, the shutdown separators caused a sharp and irreversible rise in impedance of the cell. Single layer PE separators were effective up to around 145 °C, above which they demonstrated a meltdown effect. Trilayer separators had meltdown temperatures as high as 160 °C because of the presence of additional layers of higher melting PP. It was found that the separators are not able to shutdown the cell completely. In the case of an overcharged test, the cell could continue to charge at lower currents even after the shutdown event, rendering the cell a potential hazard if not disposed immediately and safely. This usually does not become an issue in commercial cells because the cell manufacturers have addressed this issue by including multiple cutoff devices within a single cell.

Development efforts are under way to displace the use of microporous membranes as battery separators and instead use gel electrolytes or polymer electrolytes. Polymer electrolytes, in particular, promise enhanced safety by eliminating organic volatile solvents. The next two sections are devoted to solid polymer and gel polymer type lithium-ion cells with focus on their separator/electrolyte requirements.

6.2. Lithium Polymer

Because of their high theoretical capacity, lithium polymer batteries have long been identified as a very promising technology to meet the requirements of upcoming applications such as standby power and electric vehicles. Research and development of polymer electrolytes for ambient-temperature rechargeable lithium batteries has always been very active. Rapid progress for the past 2 decades in this field has led to numerous monographs and reviews.[131−137] These polymers are generally polyethers, poly(ethylene oxide) (PEO), or poly(propylene oxide) (PPO).

Solid polymer electrolytes serve two principal roles in rechargeable lithium batteries. Not only do they function as the traditional electrolyte, i.e., the medium for ionic transport but also they function as the separator which insulates the cathode from the anode. Consequently, the polymer electrolyte must have sufficient mechanical integrity to withstand electrode stack pressure and stresses caused by dimensional changes, which the rechargeable electrodes undergo during charge/discharge cycling.

Lithium polymer electrolytes formed by dissolving a lithium salt LiX (where X is preferably a large soft anion) in poly(ethylene oxide) PEO can find useful application as separators in lithium rechargeable polymer batteries.[138−140] Thin films must be used due to the relatively high ionic resistivity of these polymers. For example, the lithium-ion conductivity of PEO−Li salt complexes at 100 °C is still only about $^{1}/_{100}$th the conductivity of a typical aqueous solution.

A polymer electrolyte with acceptable conductivity, mechanical properties and electrochemical stability has yet to be developed and commercialized on a large scale. The main issues which are still to be resolved for a completely successful operation of these materials are the reactivity of their interface with the lithium metal electrode and the decay of their conductivity at temperatures below 70 °C. Croce et al. found an effective approach for reaching both of these goals by dispersing low particle size ceramic powders in the polymer electrolyte bulk.[141,142] They claimed that this new "nanocomposite polymer electrolytes" had a very stable lithium electrode interface and an enhanced ionic conductivity at low temperature, combined with good mechanical properties. Fan et al.[143] has also developed a new type of composite electrolyte by dispersing fumed silica into low to moderate molecular weight PEO.

The gel type polymer electrolyte prepared by dispersing ceramic powders (e.g., Al_2O_3) into a matrix formed by a lithium salt solution contained in a poly(acrylonitrile) (PAN) network was reported by Appetecchi et al.[144] These new types of composite gel electrolytes had high ionic conductivity, wide electrochemical stability, and particularly, high chemical integrity even at temperatures above ambient. Kim et al.[145] used a blend of PVdF−HFP and PAN as a matrix polymer to attain high ionic conductivity and good mechanical strength. The PAN can give mechanical integrity and structural rigidity to a porous membrane without inorganic fillers. The high ionic conductivity was due to the high volume of pores and a high affinity of the membrane for electrolyte solution.[146]

6.3. Lithium-Ion Gel Polymer

The solid polymer electrolyte approach provides enhanced safety, but the poor ambient temperature conductivity excludes their use for battery applications, which require good ambient temperature performance. In contrast, the liquid lithium-ion technology provides better performance over a wider temperature range, but electrolyte leakage remains a constant risk. Midway between the solid polymer electrolyte and the liquid electrolyte is the "hybrid polymer" electrolyte concept leading to the so-called gel polymer lithium-ion batteries. Gel electrolyte is a two-component system, viz., a polymer matrix swollen with a liquid electrolyte. The gel polymer electrolyte approach to the lithium-ion technology combines the positive attributes of both the liquid (high ionic conductivity) and solid polymer electrolytes (elimination of leakage problems).

Gel polymer lithium-ion batteries replace the conventional liquid electrolytes with an advanced polymer electrolyte membrane. These cells can be packed in lightweight plastic packages as they do not have any free electrolytes and they can be fabricated in any desired shape and size. They are now increasingly becoming an alternative to liquid-electrolyte lithium-ion batteries, and several battery manufacturers, such as Sanyo, Sony, and Panasonic have started commercial production.[147,148] Song et al.[149] have recently reviewed the present state of gel-type polymer electrolyte technology for lithium-ion batteries. They focused on four plasticized systems, which have received particular attention from a practical viewpoint, i.e., poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN),[150] poly(methyl methacrylate) (PMMA),[151,152] and poly(vinylidene fluoride) (PVdF) based electrolytes.[153−157]

One particular version of the lithium-ion gel polymer cells, also known as plastic lithium-ion cell (PLION), was developed by Bellcore (now Telcordia Technologies).[158−160] In this case, Gozdz et al. developed a microporous plasticized PVdF−HFP based polymer electrolyte which served both as separator and electrolyte. In PLION cells, the anode and cathode are laminated onto either side of the gellable membrane. Good adhesion between the electrodes and the membranes is possible because all three sheets contain significant amounts of a PVdF copolymer that can be melted and bonded during the lamination step.

The PVdF−HFP separators used in PLION cells were around 3 mil thick, and had poor mechanical properties. It has been reported that the major source of rate limitation in PLION cells was the separator thickness.[161] The rate capability of these cells can be significantly improved by decreasing the separator thickness to that typically used in liquid electrolyte system. Moreover, in the absence of shutdown function, the separator does not contribute to cell safety in any way. Park et al. reported that the HFP content in separators did not have any significant impact on cell performance.[162] The Bellcore process has proven to be an elegant laboratory process but is difficult to implement in large-scale production.

To overcome the poor mechanical properties of polymer and gel polymer type electrolytes, microporous membranes impregnated with gel polymer electrolytes, such as PVdF, PVdF−HFP, and other gelling agents, have been developed as an electrolyte material for lithium batteries.[163−173] Gel coated and/or gel-filled separators have some characteristics that may be harder to achieve in the separator-free gel electrolytes. For example, they can offer much better protection against internal shorts when compared to gel electrolytes and can therefore help in reducing the overall thickness of the electrolyte layer. In addition the ability of some separators to shutdown

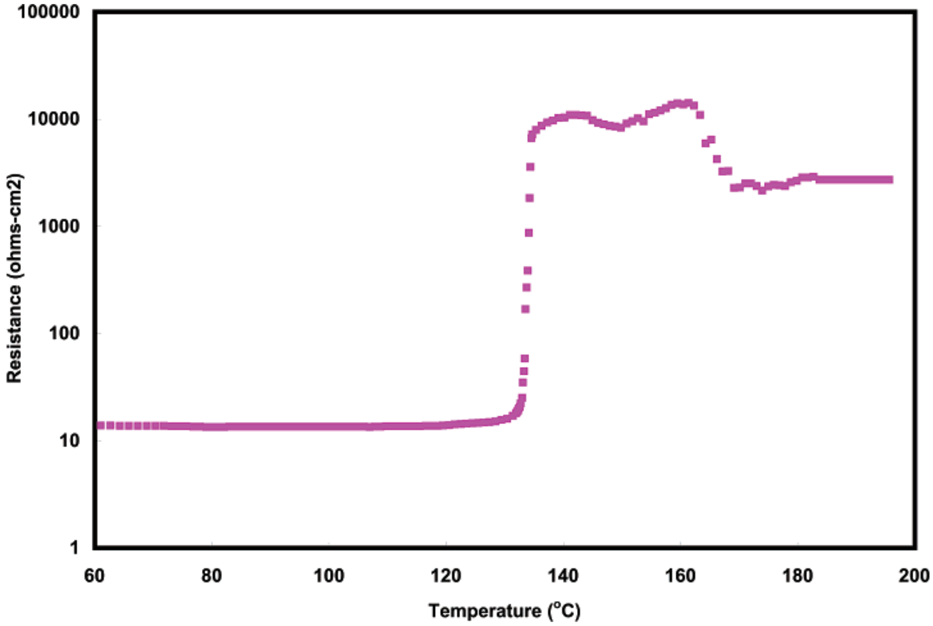

Figure 13. Internal impedance (at 1 kHz) of PVdF coated Celgard trilayer separators as a function of temperature. Heating rate: 60 °C/min.

at a particular temperature allows safe deactivation of the cell under overcharge conditions.

The shutdown behavior of PVdF coated Celgard trilayer membranes is shown in Figure 13. The shutdown is defined by the sharp increase in resistance around 130 °C. The PVdF coating should be porous and should not block the pores to maintain similar ionic conductivity. The scanning electron micrographs of the PVdF coated membrane is shown in Figure 14. The cross section SEM of Celgard 3300 provides visual evidence that the coating is porous and is not blocking the pores of the top PP layer.

Abraham et al.[174] were the first ones to propose saturating commercially available microporous polyolefin separators (e.g., Celgard) with a solution of lithium salt in a photopolymerizable monomer and a nonvolatile electrolyte solvent. The resulting batteries exhibited a low discharge rate capability due to the significant occlusion of the pores with the polymer binder and the low ionic conductivity of this plasticized electrolyte system. Dasgupta and Jacobs[163,175] patented several variants of the process for the fabrication of bonded-electrode lithium-ion batteries, in which a microporous separator and electrode were coated with a liquid electrolyte solution, such as ethylene−propylenediene (EPDM) copolymer, and then bonded under elevated temperature and pressure conditions. This method required that the whole cell assembling process be carried out under scrupulously anhydrous conditions, which made it very difficult and expensive.

More recent methods proposed by Motorola[176,177] and Mitsubishi Electric[178] researchers differ in implementation details, but they share a common feature in that a separate adhesive layer (PVdF) is applied to the separator and used to bond the electrode and the separator films, using in the first case the hot, liquid electrolyte as an in situ PVdF plasticizer. Recently, Sony[179,180] researchers described the use of a thin, liquid electrolyte-plasticized polyacrylonitrile layer directly applied either to the electrode or the separator surfaces as an effective ion-conductive adhesive. Sanyo[181,182] investigators, on the other hand, used thermally polyerizable additives to gel, or solidify, liquid electrolyte solutions in a wound, packaged battery.

The ceramic fillers (e.g. Al_2O_3, SiO_2, TiO_2) can greatly influence the characteristics and properties of polymer electrolyte by enhancing the mechanical stability and the conductivity.[141,183−186] γ-$LiAlO_2$, Al_2O_3, and MgO were used as fillers by Prosini et al.[187] in a PVdF−HFP polymer matrix to form self-standing, intrinsically porous separators for lithium-ion batteries. The MgO based separators showed the best anode and cathode compatibilities.

Liu et al.[188] has successfully prepared a PVdF−HFP/PE composite gel electrolyte by cast method. They showed that when the PE content was over 23 wt %, the electrical impedance of the composite gel electrolyte increased rapidly by several orders of magnitude, around the melting point of PE. The SEM pictures showed that the PE particles were fused and formed into a continuous film at or near the PE melting point, which cuts off the ion diffusion. This shutdown feature of the composite gel electrolyte can help in preventing the cell runaway under abusive usage. Similarly, poly(ethylene oxide) (PEO) coated separators were prepared by Kim et al.[189] by coating PEO onto a microporous PE separators. The ionic conductivity of PEO coated membranes was higher then the base film. Kim et al. prepared the polymer electrolytes by coating poly(ethylene oxide) (PEO) and poly(ethylene glycol dimethacrylate) (PEGDMA) onto a microporous polyethylene membrane (Asahi Kasei, 25 um, 40% porosity).[190] They showed that the relative weight ratio of PEO and PEGDMA coated on to the microporous membrane played a critical role in determining the uptake of electrolyte solution and ionic conductivity.

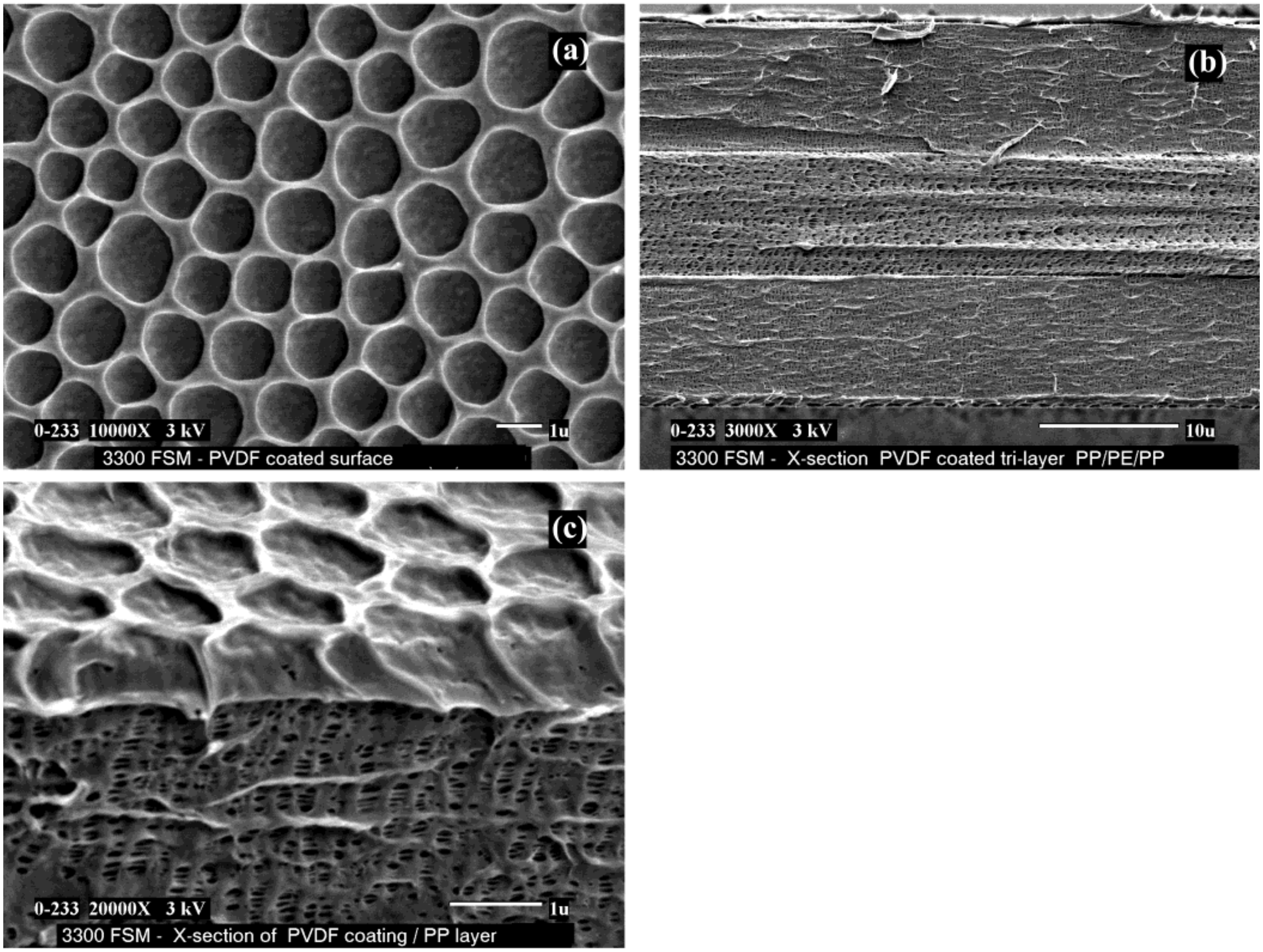

Figure 14. Scanning electron micrographs of Celgard PVdF coated separators used in lithium gel polymer batteries: (a) surface SEM, (b) cross-section SEM of coated trilayer, and (c) cross section of PVdF coating.

6.4. Lithium Primary Systems

Lithium primary batteries, with their outstanding performance and characteristics, are being used in increasing quantities in a variety of applications, including cameras, memory backup circuits, security devices, calculators, watches, etc. They were first used in early 1970s in selected military applications, but since then they have been designed using a number of different chemistries, in a variety of sizes and configurations, and have been used in different consumer applications. They are attractive because of their high voltage, high specific energy, good power density, flat discharge characteristic, good low temperature performance, and superior shelf life.

The term “lithium battery”, applies to many different types of chemistries, each using lithium as the anode but differing in cathode material, electrolyte, and chemistry as well as in design and other physical and mechanical features. Lithium primary batteries can be classified into several categories, based on the type of electrolyte (or solvent) and cathode material used—soluble cathode cells (e.g., SO_2, $SOCl_2$, SO_2Cl_2), solid cathode cells (e.g., V_2O_5, MnO_2, $(CF)_n$, FeS_x, CuO), and solid electrolyte cells (I_2 (P_2VP)). The Li–I_2 system is unique as the cell reaction product, LiI, forms the separator in situ. In the large cylindrical size batteries, three chemistries are currently available for consumer applications: Li–MnO_2, Li–CF_x, and Li–FeS_2. Li–MnO_2 and Li–CF_x cells are 3 V cells that come in special sizes and are typically used in cameras, safety devices, industrial applications, etc. Li–FeS_2 is a 1.5 V battery that is a drop-in replacement for primary alkaline and C/Zn batteries.

As the separator requirements for most of the above batteries are very similar, they will not be dealt with in detail. In this section, we will generally describe the separator requirements followed by a brief discussion on few selected systems.

6.4.1. Separator Requirements

The requirements for the separator properties are generally lower in lithium primary cells compared to lithium secondary cells. The lack of a charging process helps avoid undesirable electrochemical deposits (e.g., dendrites) as well as the generation of oxidizing substances. The mechanical strength requirements are less severe because the negative electrode is made of lithium foil, which is relatively smooth. Further, the shutdown behavior of separator is not mandatory because the thermal runaway occurs only when the cell temperatures goes beyond 180 °C (melting point of lithium). The basic require-

Table 8. Separators and Their Manufacturers for Major Primary Lithium Battery Systems

battery system	type of separator	compositions (manufacturer)
Li/SO_2	microporous	glass fiber;[a] polypropylene;[b] Tefzel
$Li/SOCl_2$	microporous	glass fiber;[c] glass mat or filter paper
Li/MnO_2	microporous	polypropylene[d] (Celgard); polyethylene (Asahi Kasei)
$Li/(CF)_n$	microporous	polypropylene[e]
Li/CuO	microporous	nonwoven glass
Li/V_6O_{13}	microporous	polypropylene (Celgard 2400)[f]
	solid-ion conductor	poly(ethylene oxide)−lithium salt[g]
Li/V_2O_5	microporous	polypropylene[h]
Li/FeS_2	microporous	polypropylene[i]
$Li/CuCl_2$	microporous	Tefzel
solid electrolyte ($Li-I_2$ (P2VP))	solid ion conductor	LiI film (self-healing)[j]

[a] Walk, C. R. In *Lithium Batteries*; Gabano, J. P., Ed.; Academic Press: New York, 1983, p 281. [b] Linden, D.; McDonald, B. *J. Power Sources* **1980**, *5*, 35. [c] Klinedinst, K. A. *J. Electrochem. Soc.* **1984**, *131*, 492. [d] Moses, P. R.; Turchan, M. J.; Taylor, A. H.; Mank, R. M. In *Lithium Batteries;* Gabano, J. P., Ed.; Academic Press: New York, 1983, p 333. [e] Morita, A.; Iijima, T.; Fujii, T.; Ogawa, H. *J. Power Sources* **1980**, *5*, 111. [f] Abraham, K. M.; Goldman, J. L.; Holleck, G. L. *Lithium Batteries*; Venkatasetty, H. V., Ed.; The Electrochemical Society, Inc.: Pennington, NJ, 1981; p 271. [g] Armand, M. B. Second International Meeting on Lithium Batteries, Extended Abstracts No. 2, Paris, France. *Solid State Ionics* **1983**, *9/10*, 745. [h] Walk, C. R. In *Lithium Batteries*; Gabano, J. P., Ed.; Academic Press: New York, 1983, p 265. [i] Uetani, Y.; Yokoyama, K.; Okamoto, O. J. *Power Sources* **1980**, *5*, 89. [j] Liang, C. C.; Holmes, C. F. J. *Power Sources* **1980**, *5*, 3.

ments are very generic—low electrical resistance, thin, high strength, low shrinkage, relatively small pore size, and no defects. As is true for separators for use in lithium-ion batteries, all the properties of separators for primary lithium batteries should be very uniform.

The most common separator by far used in these cells is the single layer PP separator made by Celgard (Celgard 2400) as shown in Table 8.

6.4.2. Chemistries

The separators used in major lithium primary systems are listed in Table 8. The majority of the lithium primary systems shown in Table 8 use microporous membranes (single layer PP or PE) as separators. Some of the systems are discussed below.

6.4.2.1. Lithium MnO_2. The Li/MnO_2 battery is the most widely used primary lithium battery. It is used in a wide variety of applications such as long-term memory backup, safety and security devices, cameras, many consumer devices, and military electronics. It uses a lithium anode, microporous polypropylene separator impregnated with electrolyte, and MnO_2 cathode. It is available in many configurations (including coin, bobbin, spirally wound cylindrical, and prismatic configurations in multicell batteries) and in designs for low, moderate, and moderately high drain application.

The Li/MnO_2 coin cells use a lithium anode disk, which is separated from the manganese dioxide pellet cathode by a nonwoven polypropylene separator, impregnated with the electrolyte. The bobbin-type design contains a central lithium anode core surrounded by the manganese oxide cathode, separated by a polypropylene separator impregnated with the electrolyte. The bobbin design maximizes the energy density due to the use of thick electrodes and the maximum amount of active materials. In the spirally wound cells, the lithium anode and the cathode are wound together with a microporous polypropylene separator to form the jelly roll. These cells are designed for high-current pulse applications as well as continuous high-rate operation.

The lithium MnO_2 system has been preferred over lithium CF_x for the primary lithium cell market for its lower cost and essentially equivalent performance for camera (cylindrical cells), watch (coin cells), and memory applications. Dan et al. published results for an AA size rechargeable size cell based on Li/MnO_2 chemistry with energy density of 125−140 W h/kg and 280−315 W h/L. The cell used a polypropylene separator and was able to pass all safety tests (short circuit, overcharge, deep discharge, crush, and nail penetration).[191] Ikeda[192] and co-workers reported the development of “long life and high reliability Li/MnO_2 cell for back up” and demonstrated how the microporous structure of Celgard flat sheet membranes reduced self-discharge to provide reliable operation for up to 10 years.

6.4.2.2. Lithium CF_x. The Li/CF_x battery consists of a lithium anode, polycarbon monofluoride cathode, and microporous polypropylene separator saturated with organic electrolyte. These batteries are used as power sources for watches, portable calculators, memory applications, and so on.

6.4.2.3. Lithium Iron Sulfide. Energizer has marketed $Li-FeS_2$ (L91) AA-size cells since 1990.[193] These cells usually have a high surface area jellyroll construction, using pyrite (FeS_2) coated onto aluminum foil as the cathode, a polyolefin (polypropylene) microporous separator, and a lithium foil anode. This system is particularly well suited for high drain and constant power applications, where its higher operating voltage extends service time.

6.4.2.4. Lithium SO_2. The lithium SO_2 systems are mainly used in military and some industrial and space applications. This system is particularly known for its capability to handle high current and high power requirements, for its excellent low-temperature performance, and for its long shelf life. They are typically fabricated in cylindrical structure by spirally winding rectangular strips of lithium foil, a microporous polypropylene separator, the cathode electrode, and a second separator layer.

6.4.2.5. Lithium $SOCl_2$. The lithium $SOCl_2$ battery has one of the highest cell voltages (~3.6 V) and energy densities of the practical battery systems. These batteries have been fabricated in a variety of sizes and designs, ranging from wafer or coin cells with capacities as low as 400 mA h to cylindrical cells in bobbin and spirally wound electrode structures and to large 10 000 A h prismatic cells. $Li/SOCl_2$ bobbin batteries are manufactured in a cylindrical configuration. The anode is made of lithium foil, which is swaged against the inner wall of the can, the separator is made of nonwoven glass fibers, and the cathode is made of Teflon-bonded acetylene black.

6.4.2.6. Lithium TiS_2. In 1990, W. R Grace & Co developed rechargeable $Li-TiS_2$ cells with high energy density, and excellent cycle life. To improve the safety, they developed a fusible separator (SafeTsep) for use in both primary and secondary lithium batteries.[112] The separator consists of two or more microporous layers with at least one of the layers capable of transforming to a nonporous membrane at a temperature between 100 and 150 °C. The additional layers maintain the dimensional stability of the separator during this transformation.[113]

6.4.2.7. Lithium Bromine. Ultrafine porous polymer membranes were prepared by Weininger et al.[194] by adding sodium benzoate or other salts of benzoic acid to the melted polymer in a weight ratio of 70−85 parts of benzoate to 30−15 parts of polymer. The salt does not dissolve in the polymer but forms a dispersion or colloidal suspension. Processing the polymer involved milling on differential rolls with the benzoate salt at 140−160 °C for PE or 170−180 °C for PP. The mixtures are then cooled close to the softening point of the polymer and sheeted into 0.0005 in thick films. The final leaching of the sheets is done in water at 20−55 °C. The salt was generally extracted over a period of 1−16 h. However, leaching is almost complete within 5−10 min. The polymers are also irradiated with high-energy electrons of 20 Mrad at a dose rate of 10 Mrad/min before or after extraction of the salt. This irradiation step is employed to improve the thermal and mechanical properties of the porous polymer. Irradiation after leaching is more effective in strengthening mechanical and thermal properties, but by this treatment, the smallest pores are closed by cross-linking. These membranes are flexible, about 50% porous, have extremely fine pore sizes (40−120 Å), and are used as separators in rechargeable lithium bromine batteries. The lithium bromine system is not a commercial system. A lot of developmental work has gone into developing the system, but it still is not commercialized.

6.4.2.8. Lithium Iron Sulfide (High Temperature). High-temperature molten salt $Li-Al/LiCl-KCl/FeS_x$ cells are known for their high energy density and superior safety. At one point they were being actively pursued for electric vehicle and pulse-power applications. Historically, boron nitride (BN) cloth or felt has been used as the separator in flooded-electrolyte cells, while MgO pressed-powder plaques have been used in starved-electrolyte cells.

Martino et al. have demonstrated the use of BN felt separators in engineering tests.[195] They have high porosity (~90%), and hence, low ionic resistance, in addition to excellent compatibility with other cell materials at the operating temperature of 470 °C. However, this separator is too expensive and has poor mechanical properties and so cannot prevent electrode shape change during cell operation.[196]

MgO, Y_2O_3, and AIN powder-based separators are substantially less expensive.[197,198] Cell assembly with such powder separators is simple and amenable to mass production. Although powder separators were shown to maintain their integrity and conform to small dimensional changes of electrodes, their porosity (~50%) is considerably lower than that of BN felt and this drawback can limit their application to stationary load-leveling systems operating at low current densities.[197]

Shimizu et al. has developed a low-cost MgO porous particle separator, which possessed both the high porosity (~85%) of the BN felt and the high mechanical resistance of powder separators.[199] The separator was prepared by loosely sintering fine MgO powder with $Mg(NO_3)_2$ as the binder. The particles thus formed showed excellent performance as separators in $Li-Al/FeS_x$ cells.

The state of development of the BN-felt separator is more advanced than that of the MgO powder separator. However, the ceramic powder separator has the potential for lower cost than the felt separator.

7. Separator for Aqueous Batteries

The aqueous batteries use water based electrolytes (e.g., KOH electrolyte for NiCd and NiMH and H_2SO_4 electrolyte for lead acid), which are less resistive then nonaqueous electrolytes. Polyolefin materials are generally suitable for use in the manufacture of separators for these batteries, but they are not inherently wettable by aqueous electrolytes. Such electrolytes are therefore unable to penetrate the pores of a separator formed from such a material, so that ion migration through the pores in solution will not occur without modification. This problem is sometimes overcome by treating the polyolefin material with a surfactant, which allows an aqueous electrolyte to wet the material. However, such surfactant can be removed from the surfaces of the polyolefin material when electrolyte is lost from the device, for example during charging and discharging cycles, and it is not subsequently replaced on the material when the electrolyte is replenished.

This problem has also been more durably addressed by modifying the surface properties of the polyolefin materials used to form polymeric sheets, by graft-copolymerizing to those surfaces a monomeric substance which, after copolymerization, confers hydrophilic properties and, in some cases, ion exchange properties. This technique has been found to be practical when the porous substrate is formed from PE, which has been found to lend itself well to a graft-copolymerization reaction of this kind. However, it has been found that when such a reaction is attempted using polyolefin materials other than PE, the rate of the grafting reaction is reduced significantly.

Graft polymerization is a convenient method for the modification of the physical and chemical properties of polymer materials and is of particular interest for synthesis of the hydrophilic membranes. Graft copolymerization can be achieved by various methods such as an exposure to ionizing radiation or ultraviolet light and the use of chemical initiators. Ionizing radiation is one of the most promising methods because of its rapid and uniform formation of active sites for initiating grafting throughout the matrix. Under appropriate experimental conditions, modifications of polymer properties can be accomplished not only on the surface but also throughout the polymer.

There have been several reports on radiation grafting of acrylic and methacrylic acid onto various substrates. These include both the direct grafting method and the preirradiation method to synthesize ion-exchange membranes. Two cation exchange membranes modified with the carboxylic acid group for a battery separator were prepared by radiation-induced grafting of acrylic acid (AA) and methacrylic acid (MA) onto a polyethylene film by Choi et al.[200] They found that KOH diffusion flux of AA-grafted PE membrane and MA-grafted PE membrane increased with an increase in the degree of grafting. AA-grafted PE membrane had a higher diffusion flux then MA-grafted PE membrane. Electrical resistance of both membranes decreased rapidly with an increase in the degree of grafting up to 120% and then leveled off.

Battery separators having carboxylic acid group were prepared by radiation induced grafting of acrylic acid onto a polyolefin nonwoven fabric (PNF). The PNF comprised approximately 60% polyethylene and 40% polypropylene. It was found that the wetting speed, electrolyte retention, thickness, and ion-exchange capacity increased, whereas the electrical resistance decreased with increasing grafting yield.[201] The surface characteristics of the separators can also be modified by plasma discharge.

This subsequent section discusses different types of aqueous batteries and the separators used in those batteries. The recent work in the development of new separators for aqueous batteries will also be discussed in detail.

7.1. Leclanche (Zinc Carbon)

Dry cells have been well-known for over 100 years and form the technical basis of today's modern dry cell industry. Zinc carbon cells are the most widely used of all the primary batteries worldwide because of their low cost, availability, and acceptability in various situations. The two major separator types ever used or in use are gelled paste and paper coated with cereal or other gelling agents such as methylcellulose.[202] The paste type is dispensed into the zinc can, and the preformed bobbin is inserted, pushing the paste up the can walls between the zinc and the bobbin. A typical paste electrolyte uses zinc chloride, ammonium chloride, water, and starch or flour as the gelling agents. The coated-paper type uses a special paper coated with flour, starch, regenerated cellulose, or other gelling agent on one or both sides.[203] The paper selected must be of low metallic impurity. A kraft paper separator provides thinner separator spacing, lower internal resistance, and increased active materials volume.[204] One of the critical functions of the separator is to keep the zinc can surface properly wetted.

As the paste separator is relatively thick compared with the paper liner, about 10% or more manganese dioxide can be accommodated in a paper-lined cell, resulting in a proportional increase in capacity.[205] The pasted separator carbon−zinc cells were phased out more then a decade ago. All the cells made since then are paper-lined constructions.

The performance and capacity advantages of alkaline batteries vs carbon−zinc is resulting in the continuous decline of this battery. The low cost of the carbon zinc cell is a major reason for its continued use. Thus, cost is a major consideration in the development and selection of separators for this system.

7.2. Alkaline Zinc MnO_2

Since its introduction in the early 1960s, the alkaline manganese dioxide (Zn/MnO_2) cell has advanced to a dominant position in the portable battery market. It gets its name from the use of alkaline solutions as electrolyte. Alkaline cells have many acknowledged advantages over zinc−carbon, including a higher energy density, longer shelf life, superior leakage resistance, better performance in both continuous and intermittent duty cycles, and lower internal resistance, which allows them to operate at high discharge rates over a wider temperature range.

In general, alkaline MnO_2 cells use “macroporous” nonwoven separators made from fibrous materials and binders. Various blends of fibers including cellulose, synthetic fiber, such as PVA fiber, nylon rayon, etc. are used in producing this type of separator. Other types such as gelled, inorganic, and radiation-grafted separators have been tried, but they have not gained much practical use. Some of the more advanced nonwoven separators are made by coating fibers made of an acrylonitride polymer with a surface layer of an acrylic acid which has carboxyl groups, that are then mixed with polypropylene fiber and bound by a PVA fiber. The carboxyl group is partially cross-linked, resulting in swelling, but remains insoluble in the electrolyte. This demonstrates the complexity of today's separators in contrast to earlier separator materials, which were primarily cellulosic.

Techniques commonly used to produce fibrous webs include the wet laid, dry laid carded, and meltblown processes. The wet laid or paper making process is the predominant method for several reasons. The wet laid process, configured properly, allows for the blending of cellulosic and polymeric components. Also, the ability to use short cut length and fine denier fiber provides for consistent blending, uniform formation, and controlled pore structure.[12]

Because of the removal of mercury from the alkaline MnO_2 cell, there has been a re-formulation in the anode paste. Because of this change, theses cells now use a nonwoven laminated to cellophane as the separator to ensure against shorting due to zinc solubility and migration. This can lead to higher separator resistance. The key to success of such a lamination is to use an adhesive (e.g., PVA) that will not interfere with the ionic movement of the electrode. Some manufacturers of the mercury free cells use nonwoven mat of much smaller pore size made possible by the availability of 0.1−0.3 denier manmade fiber. The smaller diameter fiber allows for more uniform web formation at low ream weight and thickness resulting in improved high rate performance. Often a compromise must be struck between wicking rate and average pore size.

The rechargeable Zn−MnO_2 battery is an outgrowth of the primary battery. In these type of batteries, a “microporous” type separator is required to resist dendritic growth more likely to evolve as a result of numerous recharges. Materials like cellophane, grafted membrane, or polymeric films can be used as laminates to absorptive substrates. Another approach providing a similar effect is to coat a fibrous base with a layer of viskose. Both cellophane and viskose materials have remarkable properties in that they are electropermeable when wetted with KOH. To produce the functional laminate, the base nonwoven is designed for wicking and absorbency while the cellophane or membrane provides the short resistance. The adhesive used in laminating the separator must not adversely affect electrical resistance and should not interfere with the electrochemical behavior of the cell. On the basis of sales, the alkaline Zn−MnO_2 market is about 3−4 times larger than the lithium-ion battery market.[2] As this particular article is mainly focused on separators used in lithium-based batteries, we will not be discussing Zn−MnO_2 separators in more detail.

7.3. Lead-Acid Batteries

It has been a long time since the invention of the lead-acid battery, but it still represents the most important secondary chemical power source—both in number of types and diversity of application. The lead-acid battery has maintained its leading role for so many decades due to its competitive electrical characteristics and price and due to its adaptability to new applications. It is manufactured in a variety of sizes and designs, ranging from less than 1 to over 10 000 A h.[206]

Lead-acid batteries can be classified into three major types or categories, namely, automotive (SLI), stationary, and motive power (industrial). In addition, there are many special batteries that cannot be easily categorized as either of the above types. As these types of batteries are constructed with different materials and design to meet the requirements of their intended end uses, each requires a particular separator with specific material composition, mechanical design, and physical, chemical, and electrochemical properties that are tailored for the battery and its relevant specific uses. These batteries are generally available in flooded electrolyte or valve regulated (sealed) versions. In this section the types and properties of separators used for lead-acid batteries are reviewed. The reader is referred to recent reviews published by Boehnstedt[13,207,208] and others[209−211] for detailed descriptions of lead-acid separators.

7.3.1. Flooded Electrolyte Lead Acid

Separators currently used in lead-acid batteries can be classified based on their materials of construction into four major types: plastic (PE/silica, PVC/silica, sintered PVC), paper (phenolic resin impregnated cellulose), glass (glass fiber mat), and rubber (hard rubber/silica, flexible rubber/silica, coated rubber/silica) separators. Table 9 shows the different types of separators used in batteries along with their manufacturing process and main features. Glass, paper, and sintered PVC separators can be classified as macroporous separators having an average pore diameter greater than 10 μm while all other separators can be classified as microporous separators having an average pore diameter smaller than 1 μm. All of these separators can be utilized as leaf separators in battery construction. Polyethylene can be used also for enveloped separators around either the positive or the negative plate. The use of “envelope” separators is popular in small, sealed cells, SLI, motive power, and standby batteries to facilitate production and to control lead contamination during manufacturing.

The environment concerns surrounding the lead-acid battery (e.g., the automotive battery) have been increasing in severity in recent years. The improvements and development of the separators have proceeded in accordance with the changes in the specifications for the batteries which were first made with wooden separators (the preferred wood was Oregon cedar as it contained small amounts of lignin that enhanced the performance of lead negative), then progressed through microporous rubber separators, cellulose separators, and synthetic pulp separators (SPG) with glass mats, to PVC separators, and now polyethylene separators have evolved. This sequential change in separator technology has provided continuous improvements in the charge and discharge efficiency of batteries and has given high vehicle-starting capability and reliability. Moreover, short circuits (caused by particles of active material dislodged from the battery plates) are prevented due to the smaller pores and excellent electrochemical oxidation resistance of the PE separator. These features contributed greatly to the improvement in battery life.

Rubber separators have good voltage characteristics, the ability to retard antimony transfer, properties to retard dendrite growth, and good electrochemical compatibility.[212] Due to the hydrophilic properties of the rubber composition, the separators are highly wettable and renewable for the dry-charging process. Paik et al. showed that ACE-SIL (sulfur cured, hard rubber) separators performed well in industrial stationary or traction batteries, FLEX-SIL (electron-beam-cured, flexible rubber separator) separators are suited for deep-cycling batteries, and MICROPOR-

Table 9. Typical Separators Used in Lead-Acid Battery Systems

separator	class	manufacturing process	properties
wood	paper	cellulosic separators made from cotton linters or craft pulp and generally coated with phenolic resin for acid resistance and strength	comparatively large pore size and relatively high electrical resistance
hard-rubber[213]	rubber	made by mixing natural rubber, rehydrated precipitated silica, and sulfur, which is then extruded and calendared, vulcanized under water, and dried	finer pore diameter (0.2 μm average), relatively lower electrical resistance, excellent oxidation resistance, retards antimony transfer
flexible rubber[213]	rubber	made by mixing natural rubber, rehydrated precipitated silica, which is then extruded and calendared, irradiated with an ionizing electron beam, and dried	flexible, fine pore structure (0.06 μm average), retards antimony transfer
glass-mat rubber[213]	rubber/glass mat	made by mixing a polymeric emulsion, precipitated silica, and rubber, which is then coated on a fiberglass mat and finally cured and dried	finer pore diameter (<0.2 μm average), high porosity, excellent thermal dimensional stability
sintered PVC	plastic	made by sintering PVC powder of a particle size ranging between 10 and 20 μm	medium pore size (10−20 μm), generally good chemical resistance
synthetic PVC	plastic	made from mixture of PVC, silica fine powder, and a solvent, and then extruded, calandered, and extracted	small to medium average pore size and relatively low electrical resistance
synthetic pulp with glass mat	plastic/glass	made from blending PE synthetic pulp, synthetic fiber, and fine silica powder and then heat treated	medium pore size, low electrical resistance, and long service life at high temp; more difficult to process and assemble
polyethylene (PE)	plastic	made from a mixture of UHMW PE powder, fine silica powder and mineral oil, which is extruded as a film, calendered, and made porous by extraction	fine pore size, low electrical resistance, high puncture resisatance, and strongly resistant to oxidation
glass fiber mat	glass	deposition on a single sheet, a mixture of fibers dispersed in an aqueous solution	excellent wettability, durable in an acid environment, good resiliency, high temp stability, more difficult to process and assemble

SIL (a coated, glass mat and rubber separator) separators have been found to be good choice for high rate discharging or cranking applications and for various types of gel cells.[213] Recently Daramic DC UHMW PE has demonstrated excellent performance in these applications, as well.

Poly(vinyl chloride) (PVC) and polyethylene (PE) separators have been the most commonly used separators in automotive batteries for the last 20 years. Polyethylene separators have a narrow pore size distribution. The PVC separator is built up by sintering PVC powder in general of a particle size ranging between 10 and 20 μm. The decrease of particle size in the sintered product is negligible compared to the particle size of the raw materials. The pores are dispersed homogeneously with a medium size ranging between 10 and 20 μm. Since a PVC separator exclusively consists of PVC, it exhibits advantageously good chemical resistance against acid and alkaline solutions. Unlike PE, PVC is disadvantaged due to its brittleness. The decline in PVC separators in recent years is in part due to their tendency to yield chloride ions from chemical attack.

The battery separator currently used by most flooded cell type lead-acid battery manufacturers are of the microporous PE type. It was invented in the late 1960s by W. R. Grace & Co.[214] The term "polyethylene separators" is somewhat misleading, since such a separator consists mainly of agglomerates of precipitated silica, being held within a network of extremely long-chain UHMW PE.[215] A typical PE separator formulation comprises precipitated silica (~60 wt %), UHMW PE (~20 wt %), and mineral process oil (~15 wt %), as well as some processing aids, like antioxidants and/or proprietary surface tension modifiers.[216,217]

The microporous PE separator is commercially manufactured by passing the ingredients through a heated extruder, passing the extrudate generated by the extruder through a die and into the nip formed by two heated calendar rolls to form a continuous web, extracting a substantial amount of the processing oil from the web by use of a solvent, drying the extracted web, slitting the web into lanes of predetermined width, and winding the lanes into rolls.[216]

The PE separators have excellent microporous structure for electrolyte flow with minimal lead particle deposits; excellent ductility, strength, and toughness for envelopability and plate puncture resistance; excellent oxidation, chemical and thermal resistance to resist premature deterioration; and good manufacturability with high production efficiency and relatively low raw material cost, which reduces overall manufacturing costs.[218] The PE pocket sepa-

Table 10. Comparison of Properties of Different Separators Used in Lead-Acid Batteries

property	rubber	cellulose	PVC	PE	glass fiber
year available	1930	1945	1950	1970	1980
electrical resistance	very poor	poor	poor	very good	very good
porosity	sufficient	good	poor	good	very good
battery performance (cold crank)	poor	sufficient	sufficient	very good	very good
maximum pore size	good	poor	sufficient	very good	poor
mean pore diameter	good	poor	poor	very good	poor
purity	good	fair	good	good	good
resistance to shorting	good	poor	poor	very good	poor
corrosion resistance	very good	poor	good	very good	good
oxidation resistance	fair	poor	good	very good	very good
envelopable (sealability)	very poor	very poor	sufficient	very good	very poor
flexibility	brittle	brittle	brittle	excellent	good

ration is in almost all aspects significantly superior to leaf separation. Only PE separators can be enveloped and can develop good sealability. It has low electrical resistance, sufficient porosity, small pore size, and great resistance to both shorting and corrosion. The PE separator, by virtue of its low electrical resistance, generally provides better cold cranking performance. These separators are very flexible and offer excellent oxidation resistance if the residual oil content is controlled and/or proprietary chemical modifiers have been incorporated. A comparison of the properties of different types of separators is given in Table 10.

PE separators have contributed to improved battery specific energy and specific power, increased battery cycle life, and higher temperature operating capabilities. PE separators have gained in popularity and have generally replaced PVC, cellulose, glass fiber, and other conventional separators. The transition to microporous PE envelope separators started in the U.S. in the 1970s, followed by Europe in 1980s. Today, PE separators have captured almost 100% of the U.S. market and more than 70% of the remaining worldwide automotive markets.[219]

In a flooded cell type lead-acid battery, the battery separator typically has “ribs” or protrusions extending from at least one planar face of the separator. Such ribs are either formed integrally with the backweb of the separator or can be subsequently applied to the backweb as a bead of same or different material as the backweb, or they can be formed by embossing the backweb. The ribs function is to provide proper spacing between the plates and to provide a space wherein free electrolyte resides. The ribs also provides pressure to hold the electrodes in contact with the separator. This reduces the need for precise dimensional control on the cell components. Microporous PE separators typically have a configuration comprising a backweb having a predetermined thickness and a plurality of parallel or patterned ribs spaced apart by a predetermined distance and extending outwardly from one planar surface of the backweb. The ribs extend continuously in a longitudinal direction parallel to the edges of the separator material. The thickness of the backweb and height and spacing of the ribs is specified to the separator manufacturer by the battery manufacturer; based on specifications designed to maximize certain battery characteristics desired by the battery manufacturer. SLI batteries tend to have separators that are thinner than “industrial” lead-acid batteries used for standby power sources and traction devices.

Endoh[220] has reported that one reason for the occasionally shortened life of batteries assembled with PE pocket separators is the development of internal short circuits at the bottom part of the PE separator due to anodic corrosion causing active material to shed from the positive plates and leak through the separators. He also found that when synthetic pulp (SP) separators with glass mats are used, it is possible not only to restrain the shedding from positive plates but also to protect the separators against intensive oxidation so that no internal short circuits take place. He concluded that the use of SP separators with a glass mat is required to produce long service-life batteries, especially in tropical regions.

Higashi et al.[221] carried out endurance test under high-temperature conditions on automotive batteries made with three different types of separators. One group was assembled with PE pocket separators for the negative plates, another with PE pocket separators with glass mats for the positive plates, and a third with leaf-type synthetic pulp separators with glass mats. They concluded that battery assembly with PE pocket separators with a glass mat is an effective way to achieve good endurance (i.e. life extension at high temperature), and leaf-type synthetic pulp separators with glass mats are the best approach for hot climatic conditions.

7.3.2. Valve Regulated Lead Acid (VRLA)

An important development in lead-acid battery technology is the valve regulated lead-acid battery. These batteries operate on the principle of oxygen recombination, using a “starved” or immobilized electrolyte. The oxygen generated at the positive electrode during charge can, in these battery designs, diffuse to the negative electrode, where it can react, in the presence of sulfuric acid, with freshly formed lead. The separator material should provide innumerable gas channels between the plates through which oxygen can migrate from the positive to the negative electrode. These batteries differ from its flooded electrolyte precursor in a number of important ways.[222] They have been manufactured for many years with microfiber glass separators, also called absorptive glass mat (AGM). They are inherently resistant to acid stratification and have the additional important advantage of being essentially

Table 11. Separators and Their Manufacturers for Nickel and Zinc Based Battery Systems

battery system	type of separator	manufacturer and composition
nickel−cadmium	microporous	nylon, Pellon 2505, Polypropylene
nickel−metal hydride	microporous	polypropylene (Scimat, Freudenberg)
nickel−hydrogen	microporous	polymer-inorganic compounds, asbestos, zirconium oxide cloth, Celgard 3501, polypropylene
nickel−zinc	supported liquid membrane, microporous, ion-exchange	polypropylene (Celgard 3400, 3501), PVA
silver−zinc	ion exchange	Permion (RAI); Silvergard (RAI); cross-linked PVA
	microporous	pellon, cellophane, Celgard 3400
zinc−HgO	microporous	cellulose, poly(vinyl alcohol), polyolefins, poly(vinyl chloride)
zinc−air	ion-exchange	PVA cross-linked with dimethylolurea
	microporous	asbestos, nonwoven/polypropylene laminate
zinc/bromine	microporous	polyolefins (Daramic)
	ion-exchange	nafion (DuPont)

maintenance free. The separator is a crucial component in determining the useful life of a VRLA cell. While a prime function of the VRLA cell separator is to hold the cell's electrolyte in place, it must also offer characteristics that prevent major failure mechanisms occurring in the cell's positive and negative plates.

The microglass separator, since its discovery by McClelland and Devitt, has been the material of choice for VRLA designs.[223,224] It is a wet laid nonwoven (glass fiber) "paper" and is manufactured on a paper machine. The type of paper machine used by the manufacturer can influence the separator properties. Three properties—porosity, uniformity, and fiber directionality—are important attributes that can be influenced by the type of fiber used. The glass fiber, which has a zero contact angle with the acid, is durable in the acid environment, and the fine fiber structure also has good resiliency to allow for a sustained pressure against the plate. The microglass separator has a high porosity in the 90−95% range and is very conformable. The separator can adapt to imperfections in the plate surface. The separator also has high-temperature stability. Recent studies have shown that higher levels of fine fiber and higher separator compression provide improved cycle performance in VRLA batteries.[225−228]

On the other hand, AGM separators offer little control over the oxygen transport rate or the recombination process. The arrival of too much oxygen to the negative plate could result in overheating, hindrance of the battery's ability to recharge, or even a loss of capacity. Furthermore, AGM separators exhibit low puncture resistance.

7.4. Nickel Systems

The nickel-based systems include the flowing systems: nickel−iron (Ni/Fe), nickel−cadmium (NiCd), nickel−metal hydrides (NiMH), nickel−hydrogen (Ni/H_2), and nickel−zinc (Ni/Zn). All nickel systems are based on the use of a nickel oxide active material (undergoing one valence change from charge to discharge or vice versa). The electrodes can be pocket type, sintered type, fibrous type, foam type, pasted type, or plastic roll-bonded type. All systems use an alkaline electrolyte, KOH.

The separators may be simple absorbent material except in Ni/Zn where zinc solubility creates zinc electrode shape change and zinc dendrites, resulting in shorts. The fundamental cause for zinc electrode shape change is nonuniform current distribution across the electrode surface. This leads to concentration gradients, which in turn give rise to densification and dendrite formation. In the other systems, solubility of the negative materials is minimal, and therefore, failure by shorting is nonexistent or delayed for a large number of cycles. The vented Ni/Fe, Ni/Cd, and Ni/Zn cells are mostly constructed in a prismatic configuration. Systems built in a sealed cylindrical pressurized configuration are NiCd, NiMH, and Ni−H_2. The pressure configuration in the NiCd and NiMH differs from the Ni−H_2. In the former, pressure is used to hold the electrodes and separator in contact. In the latter pressure is the result of storage of a gaseous reactant. The type of separators and their manufacturers for nickel-based systems are listed in Table 11

7.4.1. Nickel–Cadmium

The NiCd secondary battery is the most popular alkaline secondary battery, and it is available in several cell designs and in a wide range of sizes. It is a very reliable, sturdy, long-life battery, which can be operated effectively at relatively high discharge rates and over a wide temperature range.

7.4.1.1. Vented NiCd. The vented NiCd battery is one of the best-known power sources in the commercial and military fields, particularly for aircraft and communication applications. It has excellent high rate and low temperature performance capabilities. It also has a long useful life capability and is both physically and electrochemically rugged.

Early separators used in NiCd cells for space applications consisted of materials as ordinary as Whatman filter paper[5] and eventually nonwoven nylon felt (Pellon 2505). Pellon 2505 was more stable than cellulosic separators, but it too had stability limitations. In the late 1960s and early 1970s, nonwoven polypropylene saw limited use in NiCd cells. The PP separators were quite useful where sterilization (heating the cell to 135 °C) was required.[229,230] The major difficulty with nonwoven polypropylene was that it was only marginally wettable, and the amount of electrolyte that can be placed in the cell was limited.

In the early 1980s, Pellon Corporation (now Freudenberg) discontinued the manufacturing of Pellon 2505. This led to the qualification of Pellon

2536 in 1984 as the new separator material for the major portion of NiCd applications in the U.S.[231,232] Hughes Aircraft took a different approach by evaluating Freudenberg FS2117 (a nonwoven nylon fabric), nonwoven polypropylene impregnated with polybenzimidazole (PBI) and zirconium oxide material (Zircar) impregnated with either PBI or polysulfone (PS).[233] Their objective was to develop a separator that is chemically stable for a minimum of 10 years and has a better electrolyte retention and gas permeability than the state-of-the-art Pellon 2505 separator. The main purpose of the polymer impregnation of the zirconia material was to improve the mechanical strength of the fabric, which was too fragile for easy handling in the fabrication of the NiCd cells. The purpose of the PBI impregnation of the polypropylene felt was to improve the wettability in the electrolyte. They found that Zircar impregnated with PBI was the best separator for geosynchronous orbit applications while Zircar impregnated with PS was best for low earth orbit applications. The PP impregnated with PBI found to be as good as Pellon 2505 separator in some cell designs but had longer life because of excellent chemical stability and was additionally less expensive than zirconia material.

The separator used in vented NiCd's is a thin, multiple ply combination. It consists of a cloth (woven or felted nylon) that electrically separates the positive and negative plates and an ion-permeable plastic membrane (microporous polypropylene, Celgard 3400, a wettable variant of Celgard 2400) that serves as the gas barrier. This thin gas barrier, which becomes relatively soft when wetted, is frequently placed between two layers of cloth separators and receives significant mechanical support from them. Previously, cellophane has also been used as the gas barrier layer. Studies done by Hill[234] and Feldman and Verville[235] showed superior performance of NiCd batteries with Celgard microporous polypropylene separators as compared to cellophane. The authors attribute this improvement to the better chemical and thermal stability of the polyolefin sheet membrane. The outer nylon separator degrades with use by undergoing hydrolysis in the KOH electrolyte, thus seriously degrading the battery life.[236] It involves a slow hydrolysis reaction followed by fast electrochemical oxidations of the hydrolysis reaction products.

7.4.1.2. Sealed NiCd. In sealed cells, the positive and negative electrodes are wound together in a jelly roll with a separator material between them. The working principle of sealed NiCd batteries is based on internal oxygen consumption. As a prerequisite the separator has to be permeable to gaseous oxygen, which is achieved by separator pores being of a specific minimum size and not all of them being filled with electrolyte at the same time, so as to leave some gas channels. Nonwovens (fleeces) made of polyamide, PE, and PP fibers have proven themselves in these cells. With their porosity they can absorb sufficient electrolyte, and due to their pore size distribution, they can simultaneously bind electrolyte and allow oxygen transfer.

Mechanical strength is an important criterion for sealed NiCd cells, because wound cells (spiral type construction) are manufactured automatically at very high speeds. Melt blown PP fleeces, with their excellent tensile properties, are good for these cells. Frequently two layers of the same or different materials are used, to gain increased protection against shorts. For higher temperature applications (up to about 60 °C) PP fleeces are preferred since they offer better chemical stability, though at lower electrolyte absorption.[12]

The nylon-based separators tend to degrade by undergoing hydrolysis in the KOH electrolyte. The products formed by the hydrolysis reaction are believed to cause a charge imbalance between positive and negative electrodes in a sealed NiCd cell leading to a loss of overcharge protection. The harmful products include carbonates, which accumulate in the electrolyte. The nylon degradation also gives rise to ammonia and hydroxylamine redox couple, which can increase the self-discharge rate. The rate of the hydrolysis of Nylon-66 separator material was approximately one-half of that of the nylon-6 material.[237] It is well-known that in sealed NiCd cells a separator weight loss of 10% is often sufficient to cause internal shorting.[238]

7.4.2. Nickel–Metal Hydride

The sealed nickel−metal hydride battery has characteristics very similar to those of the sealed NiCd battery. The main difference is that the NiMH battery uses hydrogen, absorbed in a metal alloy, for the active negative material in place of the cadmium used in the NiCd battery. The NiMH batteries have a higher energy density and are considered more environmentally friendly than the NiCd battery. The sealed NiMH battery, however, does not have the very high rate capability of NiCd battery, and is less tolerant of overcharge.

The self-discharge rate of a Ni/MH battery is generally much higher than that of NiCd battery, especially when conventional nylon separators are used.[239] The presence of oxygen and hydrogen gases cause the polyamide materials to decompose, producing corrosion products which poison the nickel hydroxide, promoting premature oxygen evolution and also forming compounds capable of a redox shuttle between the two electrodes which further increases the rate of self-discharge.[240] In the case of the NiMH battery, ammonia and amine participate in the shuttle reaction in the same way that the nitrate ion does in the NiCd battery.

Ikoma et al. carried out a detailed investigation to study the self-discharge mechanism and contribution of separators.[241] They used nonwoven fabric made of conventional polyamide (PA), PP (with surfactant), and a nonwoven fabric whose main material was sulfonated-PP (hydrophilic) as separators. When nonwoven fabric made of chemically stable sulfonated-PP is used as a separator instead of a conventional polyamide separator, the self-discharge rate of the NiMH battery was strongly depressed, to the same level as that of NiCd battery.[240,242,243]

Recently Nagarajan et al.[244] characterized three different commercial AA cells and compared the materials and cell performance. They used a differential scanning calorimeter (DSC) to determine the materials used as separators. Toshiba cells contained both polyethylene and polypropylene, while the Sanyo and Matsushita cells separators were identified as nonwoven fabrics fabricated from conventional polyamide. Since the Sanyo and Matsushita cells used the conventional polyamide separator, the self-discharge in these cells was substantially higher due to the shuttle reaction of the ammonia and amine, which expedite self-discharge. They also characterized the commercial cells and determined that separators contribution to the overall weight of the AA cell was around 3%.

Scimat Ltd. has shown that acrylic acid grafted nonwoven polyolefin separators have the ability to absorb chemical impurities, for example ammonia, from the alkaline environments. It has been shown that by using a grafted polyolefin separator, the free ammonia present inside a NiMH cell is trapped by the separator, resulting in a reduction in self-discharge to levels normally associated with NiCd cells.[245] In October 2002, Scimat Ltd. announced the launch of the next generation of separators for NiMH and NiCd cells using its second-generation grafting technology.[246]

The commonly used separator material now is the surface treated polypropylene. The surface treatment helps in making the polypropylene permanently wettable. Surface treatments involve the grafting of a chemical such as acrylic acid to the base fibers to impart wettability and is accomplished using a variety of techniques such as UV or cobalt radiation. Another method of imparting wettability to the polypropylene is a sulfonation treatment where the base fiber material is exposed to fuming sulfuric acid. The separator surface is designed to be made hydrophilic to the electrolyte.

Cheng et al.[247] carried out the impedance study on a foam-type NiMH battery with nonwoven PP separator to determine the main causes of early cycle deterioration. Their data indicated that the decrease in the voltage characteristic of the battery was due to drying out of the separator that increases the ohmic resistance of the battery and that decay of the total discharge capacity is due to an inactive surface that increases the charge-transfer of the battery.

7.4.3. Nickel–Hydrogen

Nickel−hydrogen batteries offer long cycle life that exceeds that of other maintenance-free secondary battery systems and accordingly makes it suitable for many space applications. Three types of separator materials have been used for aerospace $Ni-H_2$ cells—asbestos (fuel-cell-grade asbestos paper), Zircar (untreated knit ZYK-15 Zircar cloth),[248] and nylon.[1,249] In year 2000, Japan supplied over 90% of the nickel−hydrogen battery separators globally.[250]

Fuel-cell-grade asbestos is a nonwoven fabric with a thickness of 10−15 mil. The asbestos fibers are made into a long roll of nonwoven cloth by a carding or paper-making process. Asbestos is a controversial material with respect to health considerations in addition to potentially being a source of corrosion at high temperatures. Although asbestos is still in use, there is a trend to replace it with Zircar (zirconium oxide cloth). Zircar fibrous ceramic separators are available in textile product forms (Zircar Products, Inc.). These textiles are composed of zirconium oxide fibers stabilized with approximately 10% yttrium oxide.[251] These materials offer the extreme temperature and chemical resistance of ceramic zirconia. They are constructed of essentially continuous individual filaments fabricated in flexible textile forms. Zircar has the drawback of being expensive and delicate from an assembly perspective. Aerospace cells have shown excellent medium term performances with their nylon separators, but it is known that nylon is weak in terms of its stability over time and its temperature sensitivity.[249]

Zirfon separator is a new alternative for $Ni-H_2$ batteries. It is a porous composite separator material composed of a polysulfone matrix and ZrO_2, which is present in a powder form. The manufacturing is based on the film-casting technique. It is very stable in concentrated KOH solutions at elevated temperatures. These films are around 300 μm thick.[252] SORAPEC has tested Zirfon in $Ni-H_2$ cells and has indicated that it is one of the best separators.[249]

7.5. Zinc Systems

Zinc is a nontoxic, relatively inexpensive, and abundant material. It is the most electropositive metal which is fully compatible with aqueous electrolytes. Its low (negative) electrode potential and its high hydrogen overpotential make it a very suitable negative electrode material for use in aqueous electrolytes.[253]

Although primary cells with zinc electrodes are widespread, secondary systems based on the same materials still suffer from a short lifetime arising from problems caused by zinc mass redistribution, undesirable changes in zinc morphology, and the influence of zinc ions on the opposite electrodes. Because nickel−zinc and manganese dioxide systems are otherwise suitable for electric vehicle propulsion, an effort to develop a long-lasting secondary storage battery is very desirable. One avenue would be to find a better separator for such systems. A lot of work has been done by different groups in developing new separators for zinc-based secondary systems, but none of them have been very successful in developing long cycle life zinc systems. The type of separators and their manufacturers for zinc-based systems are listed in Table 11.

7.5.1. Silver–Zinc

The first practical silver−zinc battery was developed more then 60 years ago. Since then, primary and secondary silver−zinc batteries have attracted a variety of applications due to their high specific energy, proven reliability and safety, and the highest power output per unit weight and volume of all commercially available batteries. However, they find very limited use in commercial applications, because of their high price and limited cycle life. Development of a battery separator which will improve the performance and life of zinc based alkaline cells has been and continues to be the focus of concerted efforts in many battery groups, both in industry and academia.

The separator used in silver–zinc cells should be permeable to water and hydroxyl ions, stable in strong alkaline solutions, and not oxidized by the solid silver oxide or dissolved silver ions and should retard the migration of dissolved ions to the anode.[203] A sophisticated separator system is needed to avoid short-circuits resulting from growth of dendrites.[5] Because of the slight solubility of silver oxides in alkaline electrolyte, little work had been done with zinc/silver oxide cells until 1941 when Andre[254] suggested the use of a cellophane barrier. Cellophane prevents migrating silver ions from reaching the anode[255] by reducing them to insoluble silver metal. The cellophane is oxidized and destroyed in the process, making it less effective for long-life cells. Cycle life is very limited, even with the best separators known to date.

In general, secondary silver–zinc cells require a minimum of three different separators. The inner separator, or positive interseparator, serves both as electrolyte reservoir and as a barrier to minimize oxidation of the main separator by the highly oxidative silver electrode. This separator is usually made of a relatively inert fiber such as nylon or polypropylene. The outer separator, or negative interseparator also serves as an electrolyte reservoir and can also, ideally, serve to stabilize the zinc electrode and retard zinc penetration of the main separator, thus minimizing the dendrite growth. Improvement in cell life has been reported with improved inorganic negative electrode interseparators utilizing such materials as asbestos and potassium titanate.[256] Asbestos helps in preventing or reducing the magnitude of short circuits and also acts as a silver “stopper”, but it is bulky and reacts with silver oxide. It may also contaminate the cell with iron and posts a health risk during fabrication. A potassium titanate mat helps to reduce zinc shape changes as well as the magnitude of short circuits. It is also bulky and more expensive.[1]

The primary ion exchange separator remains the key to the life of the secondary silver cell. The cellulosics (cellophane, treated cellophane, and fibrous sausage casing) are usually employed in multiple layers as the primary separators for these cells.[257] Cellophane has to be specifically treated as battery grade, meaning a very low content of glycerine (or deglycerinated), since glycerine is an organic material that causes fast degradation of the cell performance by weakening the texture of the cellulosic material under the influence of the strong oxidants (silver peroxide and silver monoxide) present in colloidal form.[258] Cellophane prevents migrating silver ions from reaching the anode by reducing them to insoluble silver metal.[259] The cellophane is oxidized and destroyed in the process, making it less effective for long-life cells. It also physically inhibits the zinc dendrite formation.[260] Cellophane film is typically drawn to a thickness of 1 mil, and usually five or six layers are used to wrap the cathode (silver plate) in the cell.[261]

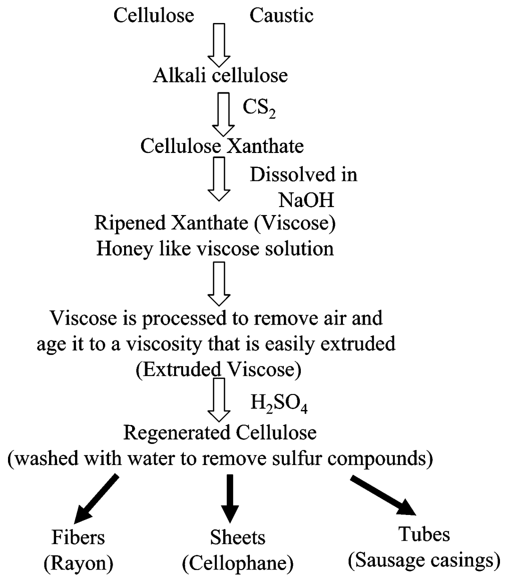

Figure 15. Viscous process for regenerated cellulose.[263]

The tendency for cellulose to degrade in alkaline solutions has been addressed by using multiple layers of the separator in the battery. Lewis et al.[262] showed that double-ply UCB cellophane films were less subject to dendritic hard shorting by zinc and retained some degree of polymerization “DP” after extended cycling. Another way to minimize cellulose degradation in alkaline solutions has been to keep the KOH concentration high (around 45%). The rate of degradation reaction slows down due to the KOH tying up the water used in the hydrolysis reaction.[263] The silver-treated cellophane gives improved life performance, reduction in rates of silver migration, and promotes a longer performance life, compared to plain cellophane.[264] However, cellophane still has significant disadvantages in terms of poor resistance to attack by the alkaline electrolyte and by active materials in the electrodes. These limit the wet life of cells, even when used in multiple layers. Cellophane is also ineffective in preventing shape change, which curtails cycle life.

Thomas Danko has described the manufacturing process and properties of cellulose in detail.[263] The term regenerated cellulose refers to cellulose that has been converted from a solubilized cellulose derivative back into a pure cellulose derivative. The most notable of these processes is the viscous process in which cellulose of fairly high DP can be dissolved and maintained at viscosities that are easy to handle (up to 300000 cps). Figure 15 describes the viscous process in detail.[263] The molecular weight of cellulose is described by the degree of polymerization (DP), which is the number of glucose units in the molecular chain. The final DP is selected based on desired properties and a balance of the regeneration process conditions. Purity of the cellulose plays an important role in the production of regenerated cellulose. The impurities (hemicellulose which is a low DP polysaccharide) in the cellulose reduces the strength of the final film. The properties of the regenerated cellulose can vary depending on the source of wood pulp used (purity) and the regeneration conditions used to convert the xanthate derivative back in to cellulose. By using a high purity wood pulp, a stronger and less porous film can be made.

For battery separators, regenerated cellulose is placed on the surface of nonwoven so that the nonwoven is available to promote the wicking of the electrolyte. The nonwovens should not allow the penetration of viscose into itself. Suitable nonwovens are made from polypropylene, poly(vinyl alcohol), and hardwood hemps. Regenerated cellulose films are commonly used in alkaline manganese cells, both primary and secondary, in NiCd industrial batteries, as well as in silver−zinc batteries.

A variety of other separators have been proposed and developed to replace or complement the cellulosics, such as poly(vinyl alcohol) (PVA),[265] radiation-grafted polyethylene,[260] microporous polypropylene, inorganic separators,[256] and other synthetic polymer membranes. The inorganic separators are stable at higher temperatures (∼150 °C), and also resist attack by silver oxides and electrolyte, but it leads to higher cell resistance and they are more expensive. Modified polyethylene films are thinner then standard materials leading to higher energy density. They also provide a greater resistance to attachment by silver oxides and electrolyte but are more expensive, more difficult to handle and provide lower resistance to zinc penetration.[1] It requires a coating of the appropriate material(s) to improve the resistance to zinc and silver.

The degradation in mechanical properties of nonwoven battery separator was studied by Danko[266] by storing the separators in 40% KOH for long period of time. The test showed that among the nonwovens, the polyamide retained about 93% of its initial tensile strength whereas poly(vinyl alcohol) and cellulosic nonwovens retained only 55% and 35%, respectively. Adding the viscose coating to the nonwovens improved tensile strength retention by 20−25% for the poly(vinyl alcohol) and cellulosic materials. The viscose-coated polyamide retained more than 98% of its initial tensile strength.

Recently Serenyl used a flexible alkaline separator (FAS) in Silver−Zinc cells, which consists of a microporous polyolefin film, with inorganic filler.[267] This can be folded around the silver and/or zinc electrodes to form conventional “U” wraps or heat sealed bags. They showed that the FAS was not attacked by the electrolyte and helps in inhibiting the “shape change” of zinc electrode.

Another commonly used alternate separator material is prepared from a radiation graft of methacrylic acid onto a polyethylene membrane such as Permion.[259] The graft makes the film wettable and permeable to the electrolyte. The low resistance Permion 2192 barrier membrane is suitable for high-rate KOH cells while higher resistance Permion 2193 is suitable for low rate NaOH cells. Cellophane is still often used in conjunction with the grafted separator as a sacrificial barrier. The lamination of cellophane to either side of the Permion membrane results in a synergistic action for stopping silver migration.[268] Lee and co-workers[269] reported that Permion extended the service life of Zn/AgO button cells from 2 to up to as much as 4−5 years. RAI Research Corporation also developed an improved ion-exchange membrane (Silvergard), which has better selectivity toward silver-ion diffusivity than other ion-exchange membranes.

7.5.2. Nickel–Zinc

The nickel−zinc (NiZn) system is attractive as a secondary cell because of its high energy density and low material cost and the low level of potential pollutants contained. The widespread use of nickel−zinc batteries, particularly as electric vehicle power sources, would be strongly enhanced by significantly extending the deep-discharge cycle life beyond the current level of 100−300 cycles.[270] Considerable work has been done in the past to develop a suitable separator for nickel− and silver−zinc batteries.[271,272] An excellent discussion of separator development is contained in a comprehensive review.[273]

These cells generally fail because of zinc dendrite shorting or zinc electrode shape changes.[274] To mitigate the problem of dendrite growth and subsequent shorting, battery separators should contain submicrometer-size pores, longer pore paths, increased thickness, and multiple layers.[275] As these solutions all lead to increased resistance losses in batteries, a compromise in the properties of separators is necessary. The separator can also influence shape change. Separators with rapid mass transfer properties will reduce the electro-osmosis effects and concentration gradients within the battery, thus slowing the rate of shape change. A lot of developmental work has been done on the nickel−zinc system, but it is still not a commercial system.

The most common material used is cellophane, which is a cellulose film, which acts as a membrane and is capable of resisting zinc penetration. The cycle life of cells utilizing this material is severely limited due to the hydrolysis of the cellophane in alkaline solution. Various methods have been tried to stabilize cellulose materials, such as chemical treatment and radiation grafting to other polymers, but none have, as of now proved economically feasible. The most successful zinc migration barrier material yet developed for the nickel−zinc battery is Celgard microporous polypropylene film.[1] It is inherently hydrophobic so it is typically treated with a wetting agent for aqueous applications.

There are two broad classes of separators employed in nickel−zinc batteries; a main separator, which exhibits resistance to dendrite penetration, and an interseparator, which principally acts as an electrolyte reservoir and wicking layer. Both main and interseparator should be resistant to chemical attack by the alkaline electrolyte and resistant to oxidative attack by nascent oxygen, permanently wettable by the electrolyte, flexible, heat sealable, tear resistant, and inexpensive.

The two basic kinds of nickel−zinc main separators are the membranes and the microporous separators. Membrane separators are those in which ionic transport occurs through the interaction of the hydrophilic groups attached to the polymer with the ionic groups in the electrolyte. Ionic transport through microporous separators, on the other hand, occurs by diffusion through discrete pores. Other than wetting, there is essentially no interaction of this type of main separator with the electrolyte.

An important advantage of the microporous separator is that it has high water and electrolyte permeability leading to less electrode shape change. They can be prepared from chemically inert polymers, and hence have good chemical and oxidation resistance. The disadvantages of the microporous membranes are risk of dendrites shorting through the discrete pores and greater scope for zinc oxide to deposit within the separator pores. Membrane separators should provide greater resistance to zinc dendrite penetration, much lower rates of active material migration away from the negative electrode, and probably no deposition of zinc oxide within the separator. Their main disadvantages are the higher rates of negative electrode shape change resulting from poor mass transfer properties and the greater vulnerability to chemical attack.[276]

Lundquist[276] compared the performance of membrane separators with microporous separators and found that the rate of zinc electrode shape change is greater in batteries with membrane separators although in either case shape change was the primary failure mode. Batteries containing separators with the lowest electrolytic resistivity and highest water permeability gave the longest cycle life. The results favored the use of microporous separators since its superior mass transfer characteristics minimize the rate of shape change.

Studies made by several authors, such as Poa,[277] Wagner,[278] and Brown,[279] have shown significant improvement in the performance of NiZn rechargeable batteries, when microporous polyolefin flat sheet membranes were used as separators. Poa and coworkers examined the diffusion of the OH^- electrolyte through candidate separator materials, including microporous polypropylene, Celgard 3501 (Celgard 2500 coated with a proprietary surfactant). The OH^- diffusional flow for Celgard 3501 was found to be greater than either the traditional swollen, nonporous cellophane separator used in the battery or a nonporous methacrylic acid grafted and cross-linked polyethylene.[277]

Krejci et al. studied the transport of zincate ions through modified microporous PP separators (Celgard 3401, Celgard 3501) using polarography and conductometry.[280] Celgard 3401 and 3501 were chosen because they are proven to have slow redistribution of zinc material, good mechanical properties, and low electrical resistivity. Soluble Nafion as an ion exchange modifying agent was applied to the PP microporous separators. They studied the influence of Nafion and surfactant (coated on 3401 and 3501) on transport of zinc ions through the membrane. It was found that the zincate ions transport through the membrane was higher for higher conductivity membranes and vice versa. Higher amounts of surfactant and Nafion coating increase both the membrane conductivity and the membrane's ability to allow zinc ions to pass.

Castle Technology Corporation had developed a supported liquid membrane battery separator to prevent zinc dendrite growth and decrease the shape changes on zinc electrode.[281] These membranes use a highly specific organic transport reagent contained in a microporous membrane support to transport hydroxyl ions while rejecting zincate ions. Several materials (polyvinyl chloride (PVC), PVC copolymer, nylon, nonwoven PP, and microporous PP) were tested, and Celgard 2500 was found to be the best material because of its larger pore size and higher porosity.

The nickel zinc system would be a suitable power source for many portable devices if the cells were tightly sealed and had a prolonged life. In sealed nickel−zinc batteries, oxygen, which is formed on the positive electrode, has to recombine with metallic zinc at the negative electrode. The microporous membrane must have some degree of permeability to oxygen.[282] Sato et al. developed a separator which consisted of nylon nonwoven cloth coated with poly(vinyl alcohol) (PVA) containing boric acid. The separator has a high ionic conductivity and is resistant to zincate ion penetration.[283]

To address the zinc dendrite problem in nickel−zinc cells, eVionyx claims to have developed a proprietary membrane system that is nonporous, has very high ionic conductivity, is of low cost, and can block zinc dendrite penetration even in high concentrations of KOH.[284−286] The polymeric membrane has an ionic species contained in a solution phase thereof. The ionic species behaves like a liquid electrolyte, while at the same time the polymer-based solid gel membrane provides a smooth impenetrable surface that allows the exchange of ions for both discharging and charging of the cell.

7.5.3. Zinc–Air

For many applications zinc−air technology offers the highest available energy density of any primary battery system. It also offers a flat discharge voltage, long shelf life, safety and ecological benefits, and low energy cost. Since these cells are open to the ambient atmosphere, a factor limiting universal applications of zinc−air technology is the trade off between long service life and maximum power capability.

The separator materials used in zinc−air batteries should be inert to oxidation, stable in cells at high potentials, chemically inert to KOH at high temperatures, have a fine porous capillary structure to hold the electrolyte in the pores (and limit diffusion of oxygen gas), have a high bubble pressure, and exhibit low electrical resistance. Usually a polypropylene membrane such as treated Celgard 2500 or Celgard 3501 is used as separator in these cells. The function of the separator is to prevent cross mixing of the positive and negative electrolytes but to still allow the transport of ions. Because of its porosity, the cationic compound produced in the anode reaction can easily pass through the separator to cathode that leads to an increased polarization and decreased capacity and battery life. The separator should be able to stop the passage of these cationic compounds to increase the cell life. The commercial Zn−air cells also use laminated separators (e.g. Celgard 4560 and Celgard 5550), which have a microporous membrane laminated with a nonwoven.

Dewi et al. used a cationic polysulfonium membrane as a separator in a zinc−air cell. They showed that the polysulfonium membranes were highly effective in preventing zinc cation permeation from the anode to the cathode compared to the commercially available PP separators.[287]

A new polymeric separator membrane has been developed for alkaline electrochemical systems (e.g. metal/air, Zn/Ni, Zn/MnO_2, Zn/HgO etc.) by Schubert et al.[288,289] It is a water-soluble copolymer of acrylic acid and sodium styrenesulfonate monomers (PAASS). The monomer ratio is varied to manipulate electrolyte absorption and ionic resistivity of the copolymer. Processes have been developed to coat PAASS onto conventional nonwoven separator papers to produce composite membranes. The monomer ratio and the coating weight can be adjusted to balance ionic resistivity and shorting protection to provide adequate overall performance. PAASS coated separators demonstrate good barrier properties to soluble zincate and silver species. Preliminary use of PAASS separator materials in a rechargeable Zn/air system showed a significant improvement in shorting protection over microporous materials such as Celgard 3401.

The primary zinc−air cells have captured the hearing aid market, but the rechargeable zinc−air battery is still in the developmental stage.

7.5.4. Zinc–Bromine

The zinc−bromine battery is an attractive technology for both utility-energy storage and electric-vehicle applications. The technology has been limited in use and not commercialized due to two major drawbacks, the tendency of zinc to form dendrites and the high solubility of bromine in the aqueous zinc bromide electrolytes. Dendritic zinc deposits could easily short circuit the cell, and the high solubility of bromine allows diffusion and direct reaction with the zinc electrode, resulting in self-discharge of the cell.

Various materials have been used as separators in zinc−bromine cells. Ideally a material is needed which allows the transport of zinc and bromide ions but does not allow the transport of aqueous bromine, polybromide ions, or complex phase structures. Ion selective membranes are more efficient at blocking transport then nonselective membranes.[290] These membranes, however, are more expensive, less durable, and more difficult to handle then microporous membranes (e.g., Daramic membranes).[291] The use of ion selective membranes can also produce problems with the balance of water between the positive and negative electrolyte flow loops. Thus, battery developers have only used nonselective microporous materials for the separator.[292]

Microporous separators have the advantage of being relatively low-cost and adequately stable in the electrolyte, but unfortunately they contribute to energy-efficiency losses in the battery. Rapid transport of bromine through microporous separators and accumulation of a bromine−oil complex in the separator lead to efficiency losses. Thus, improved separators with lower bromine mass transport and higher electrolytic conductivity would be beneficial for improving the energy efficiency of zinc−bromine batteries.

7.6. Redox Flow Batteries

The redox flow battery (RFB) concept was first proposed by L. H. Thaller at the NASA Lewis Research Center, Cleveland, OH.[293,294] Since then, it has been investigated as one of the energy storage systems for solar power, nuclear power, load leveling purposes, and electric vehicles.[295]

The all-vanadium RFB developed by the University of New South Wales has the advantage of a higher electromotive force (1.4 V in a vanadium system compared to 1.1 V in an Fe/Cr system) and a higher energy density compared with other RFB systems.[296] It employs V(II)/V(III) and V(IV)/V(V) redox couples in the negative and positive half-cell electrolytes. The ideal membrane for this system should exhibit low permeation rates of the active species to minimize self-discharge and also have low area resistivity to minimize losses in internal energy. Further, the membrane should also exhibit good chemical stability for long cycle life. The energy losses in a V−RFB are partly caused by the undesired transport of vanadium ions of different oxidation states across the membrane, which separates the anolytic from the catholytic solution in the battery system.[297]

Ion exchange membranes of cation and anion selectivity are usually used as the membrane separators for V−RFB. Commercially available cation selective CMV membrane (Asahi Glass) degrades by the fully charged anolyte,[298] but the Nafion membrane (Dupont) does not appear to degrade. However, the current efficiency of the V−RFB using Nafion decreases due to self-discharge of the vanadium ions, which permeated through the membrane.[298] Furthermore, the cost of Nafion is exceptionally high. Chlorosulfonated polyolefin membrane shows a good resistivity to oxidation and its resistivity in the RFB, almost equal to Nafion.[299] It has also been reported that a cross-linked chlorosulfonated homogeneous membrane formed by accelerated electron radiation at 2.5 Mrad/pass had a longer lifetime than the non cross-linked membrane because of the increase in the chemical stability.[300,301]

Microporous membranes perform poorly in V−RFB compared to ion exchange membranes due to their poor selectivity. Modification of low cost microporous separators to impart perm-selective properties could lead to significant cost reduction. Chieng et al. developed a composite membrane from Daramic (a microporous separator), treated with Amberlite 400CG (an ion-exchange resin), and cross-linked using divinylbenzene.[302,303] The separator selectivity was improved by partially blocking or by reducing the pore size or by incorporating some ion exchange capability to the separator. The chemical stability of the membrane was found to be excellent, and the membrane was not susceptible to fouling.[304] Sulfonation of the cross-linked Daramic separators was done to impart some cation-exchange capacity, and it was successful in reducing the amount of water transport across the membrane in V−RBC.[305] The scale-up of sulfonation process is both difficult and expensive due to the very corrosive nature of concentrated sulfuric acid. Incorporation of cation-exchange groups using poly(sodium 4-styrenesulfonate) (PSSS) has been studied, and results show that the method reduces the water transport across the membrane. The PSSS treatment step can be easily scaled up.[306]

Diffusion coefficients of vanadium ions in CMS (Neosepta made by Tokuyama Soda), CMV (Selemion made by Asahi Glass), and CMX (Neosepta made by Tokuyama Soda) cation exchange membranes were determined by measuring the ion-exchange fluxes of the vanadium ions with H_3O^+ ions using a dialysis cell.[297] The lowest diffusion coefficients were observed in the CMS membrane for all vanadium ions. CMS membranes were found to be most suitable for V−RFB, as it was expected to prevent cross contamination of vanadium ions.[307]

One of the most important requirements that must be met is the membrane's ability to prevent excessive transfer of water from one half cell to the other. The preferential transfer of water can be a problem in the vanadium battery as one half-cell (the negative half cell in the case of cation exchange membranes) is flooded and becomes diluted, while the other becomes more concentrated, adversely affecting the overall operation of the cell. Most of the membranes show good initial water transfer properties, but their performance deteriorates with exposure to the vanadium solutions. Sukkar et al.[308] evaluated various polyelectrolytes to determine whether they could improve the selectivity and stability of the membranes in the vanadium redox cell solutions. Both the cationic and anionic polyelectrolytes evaluated improved the water transfer properties of the membranes, although upon extended exposure to the vanadium electrolyte the modified membranes did not maintain their improved water transfer properties. The solvent based Nuosperse 657 modified membrane displayed exceptional properties initially but also failed to maintain its performance with extended exposure to the vanadium solutions.

Another system under investigation is the iron/chromium redox flow battery (Fe/Cr RFB) developed by NASA. The performance requirements of the membrane for Fe/Cr RFB are severe. The membrane must readily permit the passage of chloride ions, but should not allow any mixing of the chromium and iron ions. An anionic permselective membrane CDIL-AA5-LC-397, developed by Ionics, Inc., performed well in this system.[309] It was prepared by a free radical polymerization of vinylbenzyl chloride and dimethylaminoethyl methacrylate in a 1:1 molar ratio. One major issue with the anionic membranes was its increase in resistance during the time it was exposed to a ferric chloride solution. The resistance increase termed "fouling" is related to the ability of the ferric ion to form ferric chloride complexes, which are not electrically repelled by the anionic membrane. An experiment by Arnold and Assink indicated that fouling decreased when the degree of cross-linking of the anion-exchange membrane was increased.[310]

Hruska et al.[311] evaluated various microporous materials (Celgard 5511 composed of porous polypropylene and Daramic W0733 composed of porous polyethylene) to reduce the columbic efficiency loss caused by the oxidation of the iron plate. The chemical resistances of both Celgard and Daramic membranes in iron electrolytes were excellent at pH = 0. Celgard separators with very low resistivity offered some improvement in columbic efficiency but the Daramic separators gave very high columbic efficiencies in a laboratory size redox cell. Daramic separators also limited the ferric ion diffusional loss to about 3% for both charge and discharge modes of operation. Two commercial ion exchange membranes were also evaluated in this study: Neosepta ACH-45T (Tokuyama Soda Company Ltd.) and Selemion DMV (Asahi Glass Company Limited). In laboratory cells, the membranes discolored, giving evidence of deterioration, and the resistivity of the membrane increased significantly. The increased resistivity was attributed to $FeCl_4^-$ fouling. Thus, attempts at lowering the polarization by maintaining a pH differential across the cell with commercial anion membranes were unsuccessful because of membrane fouling. In spite of the poor voltaic performance of the membrane, the overall Coulombic efficiency was found to be exceptionally good.

8. Mathematical Modeling of Batteries/Separators

Computer simulations have been used as a tool for understanding and optimizing battery performance since the 1970s.[312−314] Continued progress in computational tools has enabled ever-increasing sophistication in battery modeling and a steady increase in the number of systems to which modeling has been applied. Today it is possible to obtain simulation codes for all of the major rechargeable batteries, some of which are available for free.[315]

The mathematical models of different types of batteries (lead-acid,[316,317] NiMH,[318] lithium-ion[319,320]) have been developed during the past few years.[315] This has led to a better understanding of those systems. The present models consider only the thickness and porosity of the separators. Not much work has been done in incorporating the effect of physical and chemical properties of separators on the performance and safety of batteries. This is also because the microstructure of separators and their effect on transport properties in batteries are generally known only qualitatively. A thorough understanding of the microstructure of separators would be beneficial for modeling studies and optimization of electrochemical systems. This will help in making the battery model predictions more practical and reliable.

The separator pore structure is usually very complex. It consists of a porous network of interconnected pores, which are filled with liquid electrolyte. A complete description of the pore structure would require a very intricate model. Simulations are only practically possible if the structure is represented by a simplified quasi-continuum involving a few parameters. In such an approach, the "effective" electrolytic conductivity, σ_{eff}, is often defined by[97]

$$\sigma_{\text{eff}} = \epsilon^{\alpha}\sigma_0, \quad \alpha \approx 1.5 \tag{11}$$

where σ_0 is the bulk ionic conductivity of the electrolyte, ϵ is the void volume fraction of separator filled with electrolyte, and α is the Bruggeman exponent. The general applicability of $\alpha \sim 1.5$, appears questionable because separator pores are never of an ideal shape. Fan and White[321] chose a α value of 2.5 for separators in NiCd batteries, and Doyle et al.[322] used 3.3 for lithium-ion batteries. Arora et al.[323] measured the value as 2.4 for PVdF based separators by measuring the separator and electrolyte conductivity at different salt concentrations. Doyle et al. used an even higher Bruggeman exponent of 4.5 for quantifying the ionic conductivity of their plasticized electrolyte membrane.[322]

Patel et al. showed that a Bruggeman exponent of 1.5 is often not valid for real separator materials, which do not have uniform spherical shape.[324] Porous networks based on other morphologies such as oblate (disk-type) ellipsoids or lameller increase the tortuous path for ionic conductivity and result either in a significant increase of the exponent α, or in a complete deviation from the power law. They showed that spherical or slightly prolate ellipsoidal pores should be preferred for separators, as they lead to higher ionic conductivity separators.

Tye[325] explained that separator tortuosity is a key property determining transient response of a separator and steady-state electrical measurements do not reflect the influence of tortuosity. He recommended that the *distribution of tortuosity* in separators be considered; some pores may have less tortuous paths than others. He showed mathematically that separators with identical average tortuosities and porosities could be distinguished by their unsteady-state behavior if they have different distributions of tortuosity.

Doyle et al.[322] used a mathematical model to examine the effect of separator thickness for the PVdF:HFP gel electrolyte system and found that decreasing separator thickness below 52 μm caused only a minor decrease in ohmic drop across the cell. The voltage drops in the electrodes were much more significant. Mao and White[326] developed a mathematical model for discharge of a Li/TiS$_2$ cell. Their model predicted that increasing the thickness of the separator from 25 to 100 μm decreased the discharge capacity from 95% to about 90%; further increasing separator thickness to 200 μm reduced discharge capacity to 75%. These theoretical results indicate that conventional separators (25−37 μm thick) do not significantly limit mass transfer of lithium.

The use of electroactive polymers for overcharge protection has been recently reported for lithium-ion batteries.[327,328] The electroactive polymer incorporated into a battery's separator is an attractive new option for overcharge protection. Thomas et al.[329] developed a mathematical model to explain how electroactive polymers such as polythiophene can be used to provide overcharge protection for lithium-ion batteries. The model shows that, as the cell potential exceeds the oxidation potential of the polymer, the cell is transformed, over a time scale of a few minutes, from a battery into a resistor, after which a steady-state overcharge condition is attained.

9. Summary

The ideal battery separator would be infinitesimally thin, offer no resistance to ionic transport in electrolytes, provide infinite resistance to electronic conductivity for isolation of electrodes, be highly tortuous to prevent dendritic growths, and be inert to chemical reactions. Unfortunately, in the real world the ideal case does not exist. Real world separators are electronically insulating membranes whose ionic resistivity is brought to the desired range by manipulating the membranes thickness and porosity.

It is clear that no single separator satisfies all the needs of battery designers, and compromises have to be made. It is ultimately the application that decides which separator is most suitable. We hope that this paper will be a useful tool and will help the battery manufacturers in selecting the most appropriate separators for their batteries and respective applications. The information provided is purely technical and does not include other very important parameters, such as cost of production, availability, and long-term stability.

There has been a continued demand for thinner battery separators to increase battery power and capacity. This has been especially true for lithium-ion batteries used in portable electronics. However, it is very important to ensure the continued safety of batteries, and this is where the role of the separator is greatest. Thus, it is essential to optimize all the components of battery to improve the performance while maintaining the safety of these cells. Separator manufacturers should work along with the battery manufacturers to create the next generation of batteries with increased reliability and performance, but always keeping safety in mind.

This paper has attempted to present a comprehensive review of literature on separators used in various batteries. It is evident that a wide variety of separators are available and that they are critical components in batteries. In many cases, the separator is one of the major factors limiting the life and/or performance of batteries. Consequently, development of new improved separators would be very beneficial for the advanced high capacity batteries.

10. Future Directions

Up until more recent history, most of the separators and membranes historically used had not been specifically developed for battery applications. Thus, future research should be aimed at developing separators that are specifically tailored for battery applications. The general objectives of separator research should be as follows: (a) to find new and cost-effective separators, (b) to understand the separator properties in batteries, and (c) to optimize separator properties related to specific cell performance, life, and safety. One way to achieve some of these goals will be to develop mathematical models that reflect the effects of separator resistance, thickness, pore size, shrinkage, tortuosity, and mechanical strength on the final performance and safety of batteries. The battery separators for tomorrow will demand more than just good insulation and mechanical filtration; they will require unique electrochemical properties.

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