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Evaluating the trade-off between mechanical and electrochemical performance of separators for lithium-ion batteries: Methodology and application

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HIGHLIGHTS

- Methods for mechanical properties of Li-ion battery separators critically analyzed.
- A simple and reliable method for measuring effective conductivity (MacMullin number) devised.
- Major trade-off differences of mechanical and electrochemical properties of separators shown.

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ABSTRACT

Lithium-ion batteries are in widespread use in electric vehicles and hybrid vehicles. Besides features like energy density, cost, lifetime, and recyclability the safety of a battery system is of prime importance. The separator material impacts all these properties and requires therefore an informed selection. The interplay between the mechanical and electrochemical properties as key selection criteria is investigated. Mechanical properties were investigated using tensile and puncture penetration tests at abuse relevant conditions. To investigate the electrochemical performance in terms of effective conductivity a method based on impedance spectroscopy was introduced. This methodology is applied to evaluate ten commercial separators which allows for a trade-off analysis of mechanical versus electrochemical performance. Based on the results, and in combination with other factors, this offers an effective approach to select suitable separators for automotive applications.

1. Introduction

The most important function of the separator in a battery is to avoid direct electrode contact over battery lifetime while allowing unimpeded ion transport and retaining save electronic insulation even in the event of a crash. Thus, besides guaranteeing the operation of a battery the separator also assumes an important safety function [1]. Direct contact of the electrodes, i.e., the anode and the cathode, can result in unwanted thermal runaway. Because of this, rupture or leaks in the separator, caused, e.g., by the penetration of a conductive object, have to be avoided under all circumstances. Hence, one of the separator properties should be high mechanical resistance [2–7].

Besides avoiding electron flow through the separator and direct contact between anode and cathode, the separator should be thin and highly porous to facilitate good ion exchange for optimized electrochemical performance [8,9]. Due to this fact, it is evident that it would be useful to make the separator as thin and porous as

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possible. This also leads to a minimum thickness of inactive materials in the lithium-ion cell. Particularly the requirements of mechanical strength and electrochemical performance are strongly in conflict of interest since increasing porosity requires the remaining solid material to be increasingly optimally arranged to yield yet good mechanical strength. The manufacturing process in combination with the used material will therefore lead to a trade-off between mechanical and electrical performance. Current developments in separators for Li-Ion batteries target therefore morphological, thermal, mechanical and electrochemical properties of membranes. Since price is a major boundary condition the choice of base polymer remains from a rather limited set that tends to also go towards biobased polymers. A major handle being investigated is therefore on polymer blends and composite materials with inorganic fillers for example. Both approaches may drastically alter all mentioned parameters. The advent of new types of electrolytes, for example ionic liquid based ones, brought about new challenges with regard to wettability, which is for example dealt with using surface treatment. There have been a number of very insightful reviews on different aspects of such separator developments [2,3,10–17].

To find an optimum compromise for the particular application currently a number of different separator types are available worldwide commercially and many more are under development in academic and industrial labs. Three main separator types, characterized by the manufacturing technology, are commonly used in lithium-ion cells [3,10,11]:

- Microporous polymer separators
- Nonwoven separators
- Composite separators

Hence, it would be desirable to find characteristic electrochemical and mechanical parameters for available separators and proof a possible compromise.

2. State-of-the-art

In the literature a set of characteristic parameters is used to describe the separator behavior in general [3,10,18]. About ten parameters, which are listed in Table 1, can be identified. These parameters describe in principle the mechanical, electrochemical and thermal properties of the separator.

Tensile and puncture penetration tests are often used to examine mechanical properties (see also [2,11,17,18,20]). These tests are often executed to their corresponding ASTM standard with fixed standardized test parameters. However, in safety relevant abuse conditions higher than the standardized strain rates are also relevant which have not been dealt with in the literature [21,22].

In order to classify electrochemical properties, this is effective conductivity, a range of coefficients, which are usually difficult to measure and error prone such as the MacMullin number, are known from literature [23,24]. The MacMullin number describes the resistance ratio of the separator filled with liquid electrolyte to the electrolyte in free space, $N_M = R/R_0$. Most often it is not measured directly with electrolyte but taken as proportional to air permeability expressed through the Gurley value [10,19]. The Gurley value describes how easily a gas can pass the separator as an analogy to the ion flow through the separator in the battery [4,25,26]. However, permeability is not strictly proportional to diffusivity and even more so viscous flow and therefore concluding from the Gurley value to the MacMullin number is error prone. There have been methods described for the direct measurements of fuel cell components based on impedance measurements of the electrolyte filled components including by one of the authors [23,27]. Here this method for the evaluation of separator materials is leveraged.

Other important parameters for a good ion conduction are pore size, porosity and wettability [4,9,10].

Based on publicly available data sheets, it is often difficult to compare the separators in order to find a suitable one for automotive applications and their specific requirements.

Thus, the authors devise a set of easily feasible tests and analysis methods to evaluate the trade-off between the mechanical and electrochemical requirements of separators. These are applied to a set of ten currently available multilayer, monolayer, composite, and nonwoven separators used in Li-ion batteries.

3. Evaluation methods for mechanical and electrochemical characterization

The evaluation methods are described separately for the mechanical and electrochemical characterization starting from the preparation of the specimens via the experimental test setup to the analysis methods. Aim of the evaluation methods is to obtain a quick but accurate and dependable overview off the behavior in these two main properties.

3.1. Mechanical tests

Tensile and puncture penetration tests are chosen for the mechanical characterization. The tensile tests are roughly based on the ASTM D882 “Standard Test Method for Tensile Properties of Thin Plastic Sheeting” [22] and the puncture penetration tests on ASTM F1306 “Standard Test Method for Slow Rate Penetration Resistance of Flexible Barrier Films and Laminates” [21].

Table 1
Important parameters for separator materials in modern batteries [3] (if no other specified).

Parameter[a]	Description, target value[a]	Property
Thickness	Separator thickness <25 μm	Mechanical
Tensile strength	≈95 MPa [19]	
Puncture strength	>300 g/25,4 μm	
Gurley	Air permeability ≈ 25/mil s [3]	Electrochemical
MacMullin number	Resistance ratio, ≤11	
Wettability	Fast and complete wetting in electrolytes	
Chemical stability	Long term stability in batteries, ≈10 years	
Pore size	Small pores that direct electrode contact is avoided, <1 μm	
Porosity	Volumetric separator ratio with and without pores, ≈40% [3]	
Dimensional stability	Shrinkage at 200 °C, <5%	Thermal
Shut down temperature	130 °C	Thermal

[a] More values with corresponding ASTM standard can be found in Refs. [10] and [19].