



Evaluation of polyolefin-based macroporous separators for high temperature Li-ion batteries



C. Martinez-Cisneros^{a,**}, C. Antonelli^a, B. Levenfeld^a, A. Varez^a, J-Y. Sanchez^{a,b,c,*}

^a Materials Science and Engineering Department, University Carlos III of Madrid, Spain

^b University Grenoble Alpes, LEPMI, 38000 Grenoble, France

^c CNRS, LEPMI, 38000 Grenoble, France

ARTICLE INFO

Article history:

Received 20 April 2016

Received in revised form 22 August 2016

Accepted 22 August 2016

Available online 23 August 2016

Keywords:

polymer separator
macroporous membrane
Li-ion battery
high temperature battery

ABSTRACT

Macroporous separators are critical components in liquid electrolyte batteries. Besides preventing physical contact between electrodes, they enable free ionic transport, electronic isolation and thermal shutdown. Nevertheless, separators also increase electrical resistance and takes up limited space inside the battery, affecting ionic conductivity. Widely used in lithium-ion batteries, commercial polyolefin-based separators operate in a limited temperature range, mainly ranging from -20°C to $+60^{\circ}\text{C}$. The purpose of this contribution is to assess the possibility to use these separators in lithium-ion batteries operating at extended temperatures, *i.e.* between -20°C and 120°C . For this purpose, four commercially available macroporous separators based on polyethylene and polypropylene, were investigated. To determine the effect of temperature on their performance, they were aged for one week at 120°C . Evolution of their morphology and thermomechanical behavior was investigated using XRD, SEM, DSC, TGA and DMA. The thermal aging impact on the ionic conductivity was also investigated using LP30[®] as reference electrolyte. Thermal aging, *i.e.* partial clogging of the porosity, was found to have significant effects mainly on mechanical strength, morphology and conductivity.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

In any battery, the electrolyte, an ionic conductor, is one of the main contributors to its internal resistance. As the battery performance – voltage, energy and power density – mainly depends on the negative and positive electrodes (active materials, formulation, etc.), the main function of the electrolyte relies on ensuring ionic conductivity without compromising such performance by creating thick and resistive interfaces or by producing chemical/electrochemical degradation (by-products reacting eventually with active materials). To minimize the electrolyte contribution to the battery internal resistance, its ionic conductivity must be as high as possible while its thickness should remain as low as possible. Nevertheless, such slimming could be detrimental to mechanical properties, increasing the risks of short circuits by direct contact between the electrodes. To avoid such

inconvenience, both, rechargeable and non-rechargeable batteries include a material endowed with electronic insulation properties, which allows physically separating the electrodes and preventing short circuits. In all solid-state batteries, this separation is provided by ion-conducting glasses or crystalline ceramics. Separation can be also provided by ion-conducting polymers, *i.e.* polymer electrolytes made of salts dissolved in a solvating polymer matrix. Lithium battery prototypes based on these polymer electrolytes have demonstrated good cyclability at 100% DOD (Depth of Discharge), very low self-discharge and high safety [1]. Although extensive researches [2–6] have allowed improving room temperature conductivity of these ion-conductive separators, reaching 0.1 mS/cm (at 32°C) [7], they are still insufficient to address the requirements of batteries dedicated to portable electronics. In most batteries, separation between electrodes is mainly achieved by a polymer material: the so-called separator. This separator must fulfill requirements that are sometimes antagonistic, *e.g.* providing high mechanical strength and allowing high conductivity. Although the term separator is often restricted to porous polymers, pore-free polymers can be an actual and cost-cutting alternative. Dealing with the latter, they were early proposed by Feuillade et al. [8], who 40 years ago claimed the concept of thin lithium batteries and used a variety of thermoplastic based dense membranes, *e.g.*

* Corresponding author at: Materials Science and Engineering Department, University Carlos III of Madrid, Spain.

** Corresponding author.

E-mail addresses: cymartin@ing.uc3m.es (C. Martinez-Cisneros), jeasanch@ing.uc3m.es (J-Y. Sanchez).

PAN (polyacrylonitrile) or PVdF-HFP (polyvinylidene-co-hexafluoropropene) copolymers. These membranes were swollen by a liquid electrolyte, leading to what has been called plasticized polymer electrolyte (PPE), gelled polymer electrolyte (GPE) or hybrid polymer electrolyte (HPE). However, since a decrease in melting and glass transition temperatures is commonly observed after swelling the polymer matrix by the liquid electrolyte, the first denomination is usually preferred. Indeed, gel formation (GPE) occurs very rarely and HPE formulation involves, concomitantly, macromolecular and molecular solvents such as POE poly(oxyethylene) swelled by liquid electrolytes [9]. Feuillade et al. [8] early pointed out the instability of PAN versus lithium metal, which was later confirmed by Scrosati et al. [10]. This instability, ascribed to the hydrogen in alpha position of the nitrile [11], can be overcome by substituting the PAN tertiary hydrogen by a methyl, e.g. polymethacrylonitrile (PMAN). Owing to hydrogen bonding, PAN forms a gel in current liquid electrolytes, while PMAN homo- and copolymers dissolve, requiring membrane cross-linking. Despite its instability in reduction, porous PAN membranes were prepared by phase inversion, the authors claiming a high oxidative stability [12]. PVdF homopolymer is a semi-crystalline thermoplastic, whose crystallinity and melting temperature, T_m , depend on its head-to-tail content. It exhibits, upon its swelling in liquid electrolytes, poor conductivity, which makes it unsuitable for pore-free PPE. On the other hand, the copolymerization of VdF with HFP (unable to homopolymerize) results in copolymers VdF-HFP, whose crystallinity and T_m decrease with the HFP content, while T_g increases. Hence, VdF-HFP copolymers have been extensively used as PPE, in particular in the Post Li-Ion (PLION) battery developed by Bellcore [13]. The great discrepancy in the reported conductivity for poly(VdF-HFP)-based PPE could be ascribed to (i) the polymer grade, i.e. the HFP content, and (ii) the porosity arising from the film casting process [14,15]. Porous separators are indisputably the most widely used separators. Due to the average pore diameter, they have often been named microporous separators. Nevertheless, according to IUPAC nomenclature, “macroporous separators” is more appropriate. Indeed, IUPAC nomenclature ranks the pores according to their width (w) as micropores – $w < 2$ nm – mesopores – $2 < w < 50$ – and macropores $w > 50$ nm. Although essential for a proper battery performance and safety, separators have not given rise to extensive academic researches [16]. In particular, due to the highly difficult dissolution of polyethylene and polypropylene, academic research has not focused on the elaboration of separators based on them. On the other hand, several polymers that can be actually dissolved have been tested, mainly PVdF [17,18] or high performance polymers such as polyimides [19]. Indeed, when PVdF is not able to full fit requirements for being used as PPE, some advantage could be taken from its crystallinity and melting temperature to shaping it into macroporous separators [20,21]. The McMullins Number, N_M , of macroporous PVdF, around 3.6, enables to obtain an improved performance of Li-ion batteries dedicated to GSM applications [22]. Moreover, its affinity for cyclic and acyclic carbonates [14,17]

enhances pore-through wettability regarding usual Li-ion liquid electrolytes, which (i) limits conductivity losses and (ii) retains the liquid electrolyte into the porous structure. Nevertheless, such affinity has also a detrimental impact on mechanical strength, decreasing melting temperature, crystallinity content and glass transition temperature of the porous PVdF [14,17]. Recently, the use of PVdF/NCC nanocomposites based on NanoCrystallineCellulose led to a 300% increase in storage modulus and allowed the PVdF/NCC to be shaped into ~ 20 μm thick macroporous separators. Using this approach, the specific energy of a $\text{LiC}_6/\text{LiNMO}$ battery was increased by roughly 30% with regard to the same battery equipped with a 24 μm thick Celgard®2400 separator [23]. Nowadays, the use of commercial polyolefin-based macroporous separators has been widespread. Their assets lie on (i) excellent chemical stability, (ii) wide electrochemical stability window and (iii) high mechanical strength. Furthermore, the possibility of shutting-down resulting e.g. from polyethylene, sandwiched between two porous polypropylene, Celgard® 2325, which, upon melting, clogs the polypropylene porosity, is a safety guarantee. The solubility parameters of these hydrophobic polyolefins, very far from those of the used polar aprotic solvents, favor neither the pore wetting by the liquid electrolytes nor their retention. Their introduction in a liquid electrolyte results therefore in a substantial decrease of the ionic conductivity, MacMullins Number (N_M) ranging between 5 and 20 [24]. The main objective of this contribution is to investigate battery polymer separators able to operate in a wide temperature range, i.e. between -20 to $+120$ °C. Indeed, they could be successfully applied to direct conversion-storage of photovoltaic energy (rooftop power stations), hybridizing specifically designed batteries and solar panels. Such batteries, in particular in Middle East countries, would operate in an extended temperature range, as compared to current batteries, dedicated to portable electronics and even to electric vehicles. Due to the unusually wide operating temperature range and the long lifetime required for such batteries, binder-free solid electrodes [25], in which the negative is lithium titanate, LTO, would be preferable. Regarding electrolytes, 1) inorganic solid electrolytes should be discarded as all-solid-state batteries are currently unadapted to large surface areas, 2) solvent-free polymer electrolytes are usually disqualified because of their very low conductivity at sub-ambient temperatures and 3) due to their affinity with most of the liquid electrolytes, which results in a huge swelling even their dissolution at high temperature, PVdF based dense and porous separators should also be discarded. Therefore, in this work we have performed a comparative study of commercial polyolefin-based macroporous separators with special attention paid on their ex-situ thermal aging. Thermal, thermomechanical and structural comparisons between pristine and aged materials were performed on the selected separators. Even though LP30® electrolyte, owing to its poor thermal stability, cannot be used for this application, it was applied in this study to assess the impact of the thermal aging on conductivity of the sets electrolyte + separator. The impact of

Table 1
Main properties of separators under study according to their datasheets.

	Celgard®		Solupor®	
	2400	2325	10P05A	7P03A
Composition	Polypropylene (PP)	PP/PE/PP	Polyethylene(PE)	PE
Thickness (μm)	25	25	60	50
Porosity (%)	41	39	83	85
Pore Size (μm)	0.043	0.028	0.500	0.300
Tensile Strength, MD	1420 (Kg/cm ²)	1700 (Kg/cm ²)	20 MPa	15 MPa
Tensile Strength, TD	140 (Kg/cm ²)	150 (Kg/cm ²)	–	–

MD: machine direction; TD: transverse direction.

Download English Version:

<https://daneshyari.com/en/article/4767754>

Download Persian Version:

<https://daneshyari.com/article/4767754>

[Daneshyari.com](https://daneshyari.com)