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Porosity variation of lithium-ion battery separators under uniaxial tension

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ABSTRACT

Separators in lithium-ion batteries are susceptible to uneven distributions of deformation, which may lead to inhomogeneous porosity distribution when batteries are subject to complex external loadings. In this study, uniaxial tensile tests were performed for four types of commercial separators and the in-situ 3D Digital Image Correlation (DIC) technique was used to measure the strain fields. In order to minimise the adverse effect caused by the wrinkling in strip-shaped specimens, dogbone-shaped specimens were designed to improve the measurement consistency by avoiding the occurrences of wrinkles in wet-processed separators whose deformation response has weak anisotropy. Homogeneous strain distributions were observed in both wet- and dry-processed separators oriented in the machine direction, but two deformation mechanisms of necking were found for dry-processed separators in the transverse direction. In the range of strain between 0 and 0.5, no thickness change was found in all separators, and large in-plane Poisson's ratio (up to 1.4) was found in wet-processed separators. The relationship between longitudinal and transverse strains was determined experimentally, based on which the in-plane Poisson's ratio is expressed as a polynomial function of longitudinal strain. Finally, relationship between material porosity and longitudinal strain were determined which can provide additional information in multi-physics simulations.

Keywords: Lithium-ion battery; Separator; Digital image correlation; Poisson's ratio; Porosity; Mechanical abuse

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1. Introduction

Since Sony invented and launched its first commercial lithium-ion batteries (LIBs), this high energy secondary battery technology has been developed for over 20 years. Today, LIBs have been used widely as power sources for many applications (e.g. mobiles, grid energy storage, Electric Vehicles (EVs)) due to its advantages such as high energy density, low maintenance and variety of available types and shapes. Typically, a single LIB consists of three functional parts of cathode, anode and separator. Separator is a permeable membrane placed between anode and cathode to prevent the short circuit, meanwhile allowing the transport of ionic charge carriers [1, 2]. Separator is the most important part for the safety of LIBs, and therefore, its mechanical properties and pore characterisation have received great attentions from researchers [3].

The mechanical properties of separators have been comprehensively investigated and their constitutive models [4-10] depend on manufacturing process, environmental conditions (e.g. wet/dry [5-7], temperatures [8], charge-discharge cycles [9] and strain-rates [5, 7, 8, 10]). Engineering strains were either measured from the crosshead displacements [5, 7, 11, 12] or using digital image correlation (DIC) method [8, 10, 13-16]. DIC is a technique to measure the full-field displacement and strain by correlating the images of a tested specimen at different incremental deformation steps, which can produce high resolution deformation field on its surface [17]. As a non-destructive testing (NDT) method, DIC can avoid the errors caused by slipping and uneven deformation near the mechanical grips and provide more accurate measurements, which is particularly useful for the material tests of thin-film specimens at macroscopic level [18]. However, most of the uniaxial tensile tests of separators used DIC in 2D mode via a single camera [8, 10, 13, 14, 18], which may cause measurement errors if the camera is not perfectly perpendicular to the sample surface [19] or the sample has small out-of-plane displacements [20]. In addition, the selection of the virtual strain gauge (VSG) length area may influence the DIC measurement [21] due to the non-uniform strain distribution in the VSG length area [10]. Moreover, strip-shaped samples were used in most studies according to ASTM D882, which, however, may sometimes cause wrinkling and non-uniaxial tension stress state during a test [13, 22, 23]. To overcome the weakness of the strip-shaped sample, a dogbone-shaped specimen is designed in this study based on this standard to investigate whether it can improve the accuracy of the experiment.

Although Poisson's ratio is an important mechanical property for separator materials, there are limited publications on their experimental measurements. As the only publication based on authors' best knowledge, Yan et al. [18] found that the in-plane Poisson's ratio of monolayer polypropylene (PP) separators varies with strain, and it only obeys the elastic symmetry relationship of an orthotropic material in a very small range of strain (up to 0.01 in [18]). In constitutive models for separators, Poisson's ratio values are usually set between 0.3 and 0.5 [4, 24].

The porosity of a separator is equally important to understand its mechanical behaviours. Excessive porosity can increase the ionic conductivity [25] but will adversely influence the overheat shutdown performance [2], which is important for the safety of LIBs. The non-uniform porosity distribution will also lead to an uneven distribution of the electric current, resulting in the lithium plating and lithium dendrites [26-29]. In most previous studies, the porosity of the separators was regarded as a constant value with uniform distribution. However, it has been shown that non-uniform stress and strain distributions can be generated in LIBs under complex external loading conditions [30-33], leading to non-uniform and varying porosity in separators [34, 35], which may affect separator's electrochemical properties (e.g. tortuosity, resistance, etc.) [36] and other physical properties (e.g. permeability) at both microscopic [34] and macroscopic levels [35]. Therefore, it is necessary to understand the relationship between porosity and strain state in a separator.

In this study, uniaxial tensile tests were performed on four types of commercial separators, i.e. two typical dry-processed Celgard separators and the wet-processed Asahi Hipore separators with two different thickness values. Two specimen geometries were used to obtain full-field strains using 3D DIC measurement technique, in which different sizes of VSG were examined. In addition, the variation of the macroscopic Poisson's ratio caused by the change of pore structure is studied, and the relationship between the porosity and the tensile strain of the separators is determined. Finally, a model to describe the relationship between separator's Poisson's ratio and porosity is proposed, which can be used in analytical and numerical models.

2. Materials and methods

2.1 Materials

Commercial separators of monolayer polythene (PE) Asahi Kasei Hipore, monolayer PP Celgard 2500 and tri-layer (PP/PE/PP) Celgard 2325 were selected in this study with considering their wide usage [29] and different manufacturing methods. The Asahi Kasei Hipore samples are made by the wet-process with two thicknesses of 16 μm and 25 μm , and thus, Hipore-16 and Hipore-25 were used to represent them, respectively. The Celgard samples are all made by the dry-process method with a thickness of 25 μm . In order to find out the geometry of the thin film specimens that can give reliable results, both dogbone-shaped and strip-shaped specimens were used in this study. Based on previous studies, the rectangular thin film with the length-to-width aspect ratio greater than 3.7 can give uniaxial stress state in a uniaxial tensile test [37], and meanwhile meet the requirement of ASTM D882 standard. The specific cutting tool and the schematic of dogbone-shaped samples are shown in Figs. 1(a) and 1(b). Strip-shaped specimens were cut into 80 mm in length and 8 mm in width by Swann Morton No 10A Surgical Scalpel Blade, and the grip separation was set to be 40 mm, as shown in Fig. 1(c). To minimise the influences of the edge cutting and the localised compressive stress state near the clamped ends, the area of 25 mm $\times$ 6 mm in the centre is defined as the gauge area here. The printing paper was attached to the grip areas of specimens by super glue to prevent the specimens from tearing and slipping between the grips.

The microstructures of undeformed and deformed samples were taken using a Scanning Electron Microscope (Zeiss Sigma VP FEG SEM). A 10 nm thick layer of platinum was sputtered on the samples to avoid the charge build-up in SEM. Since it is difficult to carry out the in-situ tensile tests on separators (the electric beam can damage the new fibrils created without coating) [38], the deformed samples were imaged 4 days after the tensile test. It is noted that, after the samples were fully unloaded, they still experienced a slight recovery within 48 hours due to material's viscoelasticity, after which no further recovery can be found.

Fig. 1 (a) The dogbone cutting tool; (b) dogbone-shaped sample; (c) strip-shaped sample; (d) the DIC setup with patterned sample mounted on the pneumatic grips.

2.2 Loading and strain measurement

The strip-shaped specimens and dogbone-shaped specimens were mounted in the pneumatic grips according to ASTM D882 and loaded by an Instron loading frame with a 1000 N load cell. All experiments were conducted at room temperature in the ambient atmosphere with three repeats for both machine direction (MD) and transverse direction (TD) at a quasi-static strain-rate of 10^{-3} s^{-1} . In order to obtain accurate results from DIC, all tests were stopped when the sample was damaged or the number of recording images reached 1000.

The longitudinal and transverse strains of the specimens during testing were measured by the 3D DIC technique. To track the deformation during the test using DIC technique, random speckle patterns on the specimens were created by spraying black paint on specimen surfaces (images of the amplified specimens in the red box in Fig. 1(d)) using a 0.35 mm nozzle airbrush. The pattern motion on the surface of the specimen caused by the applied load can be tracked and correlated to the reference image, and therefore, the displacements and the strains can be calculated.

The DIC system manufactured by LaVision was set up as shown in Fig. 1(d). Unlike 2D DIC, stereo calibration was required using a small etched calibration grid before carrying out the 3D DIC experiment. The image was taken every second and the analogue outputs of load and displacement were used to synchronise the DIC and Instron loading machine. The calibration and image data were recorded by DaVis software via two Imager E-lite 5M CCD cameras (resolution of 2456 pixel $\times$ 2058 pixel) and the experimental results were processed and computed by StrainMaster software. For each experiment, six different size VSGs, ranging from 25 mm $\times$ 6 mm down to 1 mm $\times$ 2 mm, were applied in DIC analysis to explore the effects of the VSG size. The DIC resolution uncertainty was estimated to be 0.005% strain based on the strain calculations from two recorded images of the sample in still position under the same setting.

2.3 Initial porosity measurement

Porosity is defined as the ratio of the void volume to the total volume that includes the void volume and the matrix material volume of the separator. Electrolyte uptake method [39], mercury intrusion porosimetry (MIP) [1], gas pycnometry [40, 41], scanning electron microscope (SEM) [34] and X-ray computed tomography [42] were commonly used to determine the porosity of the samples. Material densities and porosities of the Celgard separators can be obtained from available data [42, 43], while material densities and the porosities of the Hipore separators were measured by the non-destructive gas (i.e. helium was used in this study) pycnometry technique using AccuPyc II 1340. The porosities of all samples were summarised and listed in Table 1. It is interesting to notice that the porosities in try-layer separator samples are different in PP and PE layers since lower porosity PP layers are designed to have better mechanical integrity and PE layer with lower melting temperature is designed to shut down the transport pathway of ionic charge carriers when thermal runaway occurs.

Table 1

Characterisations of separator samples.

Sample	Composition	Density (g cm ⁻³)		Initial porosity
		Avg	Stdev	
Celgard 2325	PP/PE/PP	0.91 [43]	-	41% (39% for PP layers, 44% for PE layer) [42]
Celgard 2500	PP	0.91 [43]	-	53% [42]
Hipore-16	PE	0.9927	0.0023	41.84%
Hipore-25	PE	0.9748	0.0013	40.79%

3. Relationship between porosity and strain under uniaxial tension

It has been shown that the Poisson's ratios of the polymer matrix of the separator is relatively high (e.g. 0.42 in [44]), which approaches to the Poisson's ratio value of 0.5 for incompressible isotropic materials. Therefore, the solid volume of the separator materials may be considered approximately as a constant during the test [35] based on the principle of mass conservation. Hence, the relationship between the current porosity Φ and the corresponding longitudinal strain ε_l of the deformed separator can be expressed as

$$\Phi(\varepsilon_l) = 1 - \frac{V_0(1 - \Phi_0)}{V(\varepsilon_l)} \quad (1)$$

where Φ_0 is the initial porosity, V_0 is the initial volume of the gauge area; $V(\varepsilon_l)$ is the current volume of the gauge area at longitudinal strain ε_l . The current volume can be calculated by multiplying the measured length, width and thickness before the occurrence of necking. The thicknesses of all samples were measured before and after test by a micrometre with 1 μm accuracy according to [2]. Interestingly, apart from the necking area of tri-layer Celgard 2325 TD sample, no thickness variation was found in all samples, which means that the thickness can be regarded as a constant until the start of necking. The details of the measurement and phenomenon can be seen in Appendix A. The in-situ length and width measurements were converted from the strain measured via 3D DIC, and Eq. (1) can be rewritten as

$$\Phi(\varepsilon_l) = 1 - \frac{l_0 w_0 (1 - \Phi_0)}{l_0 (1 + \varepsilon_l) w_0 (1 + \varepsilon_t)} = 1 - \frac{1 - \Phi_0}{(1 + \varepsilon_l)(1 + \varepsilon_t)} \quad (2)$$

where ε_t is the measured transverse strain, l_0 is the initial length and w_0 is the initial width of the gauge area. According to the definition of Poisson's ratio in the longitudinal direction, i.e. $\nu = -\varepsilon_t/\varepsilon_l$, the porosity can be finally expressed as

$$\Phi(\varepsilon_l) = 1 - \frac{1 - \Phi_0}{(1 + \varepsilon_l)(1 - \nu \varepsilon_l)} \quad (3)$$

It should be noted that the Poisson's ratio could be a variable function of the longitudinal strain, i.e. $\nu = \nu(\varepsilon_l)$.

4. Results and discussion

4.1 DIC results

The typical transverse strain vs. longitudinal strain curves are measured for all samples by applying a $25\text{ mm} \times 6\text{ mm}$ VSG in the gauge area, as shown in Fig. 2 where the error bars are determined by standard deviation. The uniaxial tensile engineering stress-strain curves for all samples are provided in [Appendix A](#).

Fig. 2 The transverse vs. longitudinal strain curves of (a) Celgard separators in MD, (b) Celgard separators in TD, (c) Hipore-16 and (d) Hipore-25.

As shown in Fig. 2, the dogbone samples generally have better repeatability than the strip ones. However, it is noted that the results of the longitudinal strain vs. transverse strain curves for dry-processed Celgard in TD have relatively large standard deviations since the

speckle patterns hidden in the wrinkle areas are not tracked effectively. According to previous study, the stretch-induced wrinkles are inevitable when a high anisotropic thin film is stretched in the low-stiffness direction [22], and this phenomenon can be observed in both dogbone and strip shapes of Celgard samples here.

For the wet-processed Hipore separators, although their TD stiffness is similar to their MD stiffness, the same wrinkling phenomenon is observed in strip samples, but no wrinkle has been found in dogbone samples, as shown in Figs. 2(c) and 2(d). In strip samples, the lateral contractions of the film caused by Poisson's effect are prevented by the clamped boundaries at two grip ends, which generate transverse compressive stress in the central area near the grips [37] and the thin film buckles to accommodate the in-plane strain incompatibility [45]. For the dogbone samples, the transverse compressive stress and the resulting buckles are localised in the wider areas near the grips, which do not extend to the gauge area. Even though the transverse compressive stress is negligible compared to the tensile stress, the produced wrinkles affect adversely the DIC results.

To investigate the influence of VSG size and the strain distribution on the samples, a parametric study of VSG and the full-field strain observation have been carried out. Fig. 3 presents the typical longitudinal strain vs. transverse strain curves obtained using different VSG sizes. The VSGs are applied to the centre of the gauge area for the specimens without apparent necking. For the specimens with noticeable necking, in order to find out the difference of the longitudinal strain vs. transverse strain relationships between the necking and other areas, the VSGs with the length of 1mm are applied to the necking area while there is no change of the other VSG sizes in other areas. The longitudinal strain vs. transverse strain curves for other samples are provided in Appendix A, which show high consistence and similar feature as Celgard 2325 MD.

As shown in Fig. 3, apart from the Celgard 2325 separators in TD, the results of other samples indicate that the relationships between longitudinal strain vs. transverse strain are almost independent of the VSG size, which means that Poisson's ratios of these samples can be determined reliably using the VSG sizes examined.

Fig. 3 The transverse strain vs. longitudinal strain curves with different VSG for (a) Celgard 2325 MD, (b) Hipore-16 TD, (c) Celgard 2500 TD, and (d) Celgard 2325 TD.

For the samples without necking, uniform distribution of both axial and transverse strains can be observed from Figs. 4(a) and 4(b), and Figs. A2 and A3 in Appendix A, which remains until failure or the end of tests, except the poor results caused by wrinkles in strip-shaped Hipore-16 TD (Fig. 4(b)). The wrinkles cause measurement errors and result in the inconsistency of the curves starting from longitudinal strain of 0.08, as shown in Fig. 3(b).

For the samples with necking appearance, two different deformation mechanisms can be observed. For the Celgard 2500 in TD, even though the high localised strains generated in the necking area (Fig. 4(c)) may cause the non-uniform distributions of longitudinal strain, it is observed from Fig. 3(c) that the relationships between transverse and longitudinal strains are insensitive to the selection of the VSG size. However, similar to strip shaped Hipore-16 TD (Fig. 3(b)), inconsistent transverse strain vs. longitudinal strain curves caused by wrinkling are also observed after longitudinal strains of dog-bone shaped sample and strip shaped sample reach 0.27 and 0.19, respectively. For the Celgard 2325 in TD, even though a similar necking phenomenon is found, Fig. 4(d) shows that the local necking strains can reach a higher value over 300% (this phenomenon has been also observed by Kalnaus et al. [10]). In addition, curves of the relationship between the transverse and longitudinal strains start to be divided into two paths when the longitudinal strain reaches 0.62 in dogbone-shaped sample and 0.54 in strip-shaped sample, as shown in Fig. 3(d), which is different from the phenomenon in strip-shaped Hipore-16 TD and Celgard 2500 TD. The curves for small VSGs with length of 1mm applied on the necking regions become consistent and converge to one path, while the curves for other VSGs converge to another path. According to the SEM images of the necking cross-section area of the tri-layer Celgard 2325 separator before test [1] and after test (as shown in Figs. 4(e) and 4(f), respectively), together with the observation of the 1/3 thickness reduction of the necking region (see in Appendix A1), it suggests that the intermediate PE layer is fractured after the start of inconsistency. Therefore, the transverse strain vs. longitudinal strain curves, obtained from small VSG length after the occurrence of inconsistency, are the curves of the separator with only two PP layers instead of the original tri-layer one.

Fig. 4 Strain distributions of (a) Celgard 2325 MD, (b) Hipore-16 TD at longitudinal strain of 0.2; the original images and the strain distributions in (c) Celgard 2500 TD, and (d) Celgard 2325 TD at the grip movement of 36mm; the SEM images of the necking cross-section areas of Celgard 2325 before tests [1] (e), and after tests (f).

The underpinning causes for the influence of VSG size and the characteristics of the curves are summarised in Table 2.

Table 2

Summary of the influence of VSG size and the underpinning causes.

Sample			Features of varying VSG curves	Causes
Celgard 2325	MD	Dogbone	Consistent	-
		Strip	Consistent	-
	TD	Dogbone	Curves for small VSG lengths converge to another path after longitudinal strain of 0.62.	Middle PE layer rupture
		Strip	Curves for small VSG lengths converge to another path after longitudinal strain of 0.54.	Middle PE layer rupture
Celgard 2500	MD	Dogbone	Consistent	-
		Strip	Consistent	-
	TD	Dogbone	Curves for small VSG lengths do not converge after longitudinal strain of 0.27.	Wrinkling
		Strip	Curves for small VSG lengths do not converge after longitudinal strain of 0.19.	Wrinkling
Hipore-16	MD	Dogbone	Consistent	-
		Strip	Consistent	-
	TD	Dogbone	Consistent	-
		Strip	Curves for small VSG lengths do not converge after longitudinal strain of 0.08.	Wrinkling
Hipore-25	MD	Dogbone	Consistent	-
		Strip	Consistent	-
	TD	Dogbone	Consistent	-
		Strip	Consistent	-

Based on the experimental results discussed in this section, video extensometer, instead of DIC, is recommended for the **uniaxial tensile test** of the samples with uniform strain distributions, which can monitor the strain results synchronously and save the post-processing time. DIC has great advantage for the analysis of complex and non-uniform strain distributions in the sample.

4.2 Poisson's ratio

It should be noted that, due to the high porosity and microstructural characterisation of the samples, the Poisson's ratio calculated based on the transverse and longitudinal strains is actually a macroscopic value, instead of an intrinsic material property. In this section, the variations of Poisson's ratio are studied for strains between 0 and 0.5. The out-of-plane (i.e. through-thickness) Poisson's ratio is taken as 0 because no thickness change is found in this

range of strain, which has been discussed in Section 4.1. However, it seems that the in-plane Poisson's ratio is related to the complex meso-scale interactions of the pore structures, and therefore, a polynomial equation of the longitudinal strain with higher orders is selected, i.e.

$$v(\varepsilon_l) = \sum_{i=0}^5 J_i (\varepsilon_l)^i \quad (4)$$

where ε_l is the longitudinal strain in the uniaxial stress state, and J_i are deformation constants obtained by fitting the experimental results. Poisson's ratio vs. strain curves are shown in Figs. 5(a) and 5(b), and as a comparison, the transverse strain vs. longitudinal strain curves are also presented (Figs. 5(c) and 5(d)). Constants J_i are summarised and listed in Table 3. The data obtained from dogbone samples with 25 mm $\times$ 6 mm VSG are used in this section.

Fig. 5 The Poisson's ratio vs. longitudinal strain curves for (a) dry-processed Celgard separators, and (b) wet-processed Asahi Hipore separators; the transverse strain vs. longitudinal strain curves for (c) dry-processed Celgard separators, and (d) wet-processed Asahi Hipore separators. (Note: Red dashed curves represent Poisson's ratio for constant volume).

Table 3

Polynomial parameters in Eq. (4).

Sample	Orientation	J_0	J_1	J_2	J_3	J_4	J_5
Celgard 2325	MD	0.174	2.744	-45.131	252.526	-611.701	553.140
	TD	0.088	1.632	-4.475	7.562	-6.671	2.265
Celgard 2500	MD	0.231	6.276	-115.174	750.556	-2135.757	2258.661
	TD	0.049	3.541	-23.205	85.843	-148.788	94.662
Hipore-16	MD	0.357	5.124	-7.655	-2.596	6.040	1.729
	TD	0.510	7.006	-17.730	18.002	-21.024	21.735

Hipore-25	MD	0.483	4.524	-6.977	-20.339	60.819	-42.666
	TD	0.225	2.146	-7.024	21.524	-35.688	21.557

As the volume can be calculated by

$$V = tlw = tl_0(1 + \varepsilon_l)w_0(1 - v\varepsilon_l) \quad (5)$$

where t is the thickness, which is approximately a constant in this case. Hence, the change of the volume is

$$dV = [1 - (2\varepsilon_l + 1)v]V_0 \quad (6)$$

and the in-plane Poisson's ratio for the zero volume change (constant volume) can be obtained by

$$v = \frac{1}{2\varepsilon_l + 1} \quad (7)$$

which means the volume decreases under tension when the in-plane Poisson's ratio is greater than $1/(2\varepsilon_l + 1)$, and volume increase when the in-plane Poisson's ratio is less than $1/(2\varepsilon_l + 1)$. In order to indicate the volume variations of the samples, the red dashed curves of $v = 1/(2\varepsilon_l + 1)$ are illustrated in Fig. 5 representing the constant volume. The experimental and polynomial fitted curves above the red dashed curves in Figs. 5(a,b) represent volume decrease under tension, while those below the red dashed curves represent volume increase under tension. Fig.5 (c,d) could be explained in a similar way.

It is shown that, for the dry-processed Celgard separators, the Poisson's ratios are fluctuated in MD and increased steadily in TD, but remain less than 0.4. However, for the wet-processed Asahi Hipore separators, large Poisson's ratios can be observed (especially for the Hipore-16 TD, which can reach 1.4 at strain around 0.3), which means that the volume is decreased under tension. This unusual phenomenon can be attributed to the pore closure phenomenon under uniaxial stretching of the wet-processed separators, which will be discussed further in Section 4.3. When the pores collapse, the void volume reduces with the negligible changes of matrix material volume and leads to the total volume decrease, which causes the occurrence of high Poisson's ratio. Therefore, even though the samples look like solid membranes, the invisible pore structures have strong influence on the transverse deformation and Poisson's ratio.

4.3 Porosity equation

Based on Eq. (3) and Eq. (4), the variation of the porosity with longitudinal strain can be rewritten as:

$$\Phi(\varepsilon_l) = 1 - \frac{1 - \Phi_0}{(1 + \varepsilon_l)(1 - \varepsilon_l \sum_{i=0}^5 J_i(\varepsilon_l)^i)} \quad (8)$$

where initial porosity Φ_0 and constants J_i are given in Table 1 and Table 3, respectively. The porosity vs. strain curves for all samples are presented in Fig. 6.

Fig. 6 The porosity vs. strain curves of (a) Celgard separators, and (b) Asahi Hipore separators.

It can be clearly seen that the porosities of the dry-processed Celgard separators increase steadily with the axial strains in both MD and TD. In the range of strain between 0 and 0.1, the porosities of all Celgard samples increase linearly with strain by around 5%. Then, the increase of porosity in MD is faster than that in TD. For the wet-processed Asahi Hipore separators, an opposite trend of porosity variation is observed compared to the dry-processed one. The porosities of all wet-processed samples increase slightly at the initial small strain, and then start to decrease with strain. Especially for the Hipore-16, the porosity is reduced significantly to less than 15% when the strain reaches 0.5. The difference in porosity variation between dry-processed and wet-processed separators is due to the different pore structures from different manufacturing processes, as shown in Fig. 7.

Fig. 7 SEM images of (a) Celgard 2325, (b) Celgard 2500, (c) Hipore-16 and (d) Hipore-25 before tensile test.

It can be clearly seen that the dry-processed separators have a split-like pore structure, which is mainly formed by the TD oriented lamellas and the MD oriented fibrils between lamellas (see Figs. 7(a) and 7(b)), while the wet-processed separators have pores formed by unoriented fibrils of different sizes (see Figs. 7(c) and 7(d)).

The phenomenon that the porosities of dry-processed separators increase with strains is supported by the interrupted in-situ tensile tests conducted by Zhu et al. [38]. When a dry-processed separator is stretched in MD, the crazing of lamellas can cause the formation of new fibrils and new pores, and no change in pore size can be found. When it is loaded along TD, no obvious new fibrils are developed, but the lamellas became thinner and the pore size is increased. Even the porous microstructures of a dry-processed separator are deformed in different ways when it is stretched in different directions, its porosities always increase as a result of increasing void volume with unchanged matrix material volume, which support the porosity equation (Eq.(5)) and the corresponding curves in Fig. 6(a).

Fig. 8 illustrates the microstructures of the deformed wet-processed separators after four days from the tensile tests (i.e. after the full recovery of the viscoelastic deformation). Although they are not the instantaneous microstructures of the sample at the end of the tensile test, the variation trends of their pore structures have no fundamental differences from the predicted results in Fig.6(b). When the Hipore-16 is stretched, the fibrils are forced to form lamellas caused by transverse shrinkage, as shown in Figs. 8(a) and 8(b). Significant pore-closure can be found in this 16 μm thick wet-processed separator sample, especially for the one stretched in TD, which have a good agreement with the results in Fig. 6(b). Compared to Hipore-16, Figs. 8(c) and 8(d) show that Hipore-25 has a minor pore-closure characterisation under tensile loading. When Hipore-25 is stretched in MD, most of the pores are getting smaller and several bundles of thin lamellas are formed by the combination of fibrils, which is similar to the Hipore-16 stretched in MD. For the Hipore-25 stretched in TD, the pores are reshaped as a result of fibrils deformation, but no significant pore-closure can be found here, which also supports the trend shown in Fig. 6(b).

Fig. 8 SEM images of after deformed samples: (a) Hipore-16 MD, (b) Hipore-16 TD, (c) Hipore-25 MD and (d) Hipore-25 TD.

Lastly, the mechanical safety of LIBs is an important issue for current industrial application such as EVs and other portable electronic products, and the separator is the most important factor to safety. Previously, studies of mechanical integrity were mostly focusing on the mechanical fracture of the separator on a macro-level when it suffered external loadings. However, when a LIB was deformed by an external loading (such as bending, crushing, etc.), deformations or strains were distributed inhomogeneously. The local uneven porosity of the separators caused by inhomogeneous strain distribution can result in non-uniform distribution of the electric current, which should be considered in multi-physics modelling.

5. Conclusions

In this study, mechanical behaviours and porosity variations of four typical types of commercial separators were investigated by uniaxial tensile tests monitored by 3D digital image correlation technique. It is found that dogbone-shaped samples had better consistent results by avoiding the appearance of wrinkling in the thin film compared to strip-shaped samples. Uniform strain distributions remain until the end of tests in both MD and TD of all wet-processed separators and in only MD of dry-processed separators while localised high strains and apparent necking are observed in TD of dry-processed separators. Three typical types of transverse strain vs. longitudinal strain curves for different virtual strain gauge (VSG) sizes are observed. For the samples without structure ruptures and wrinkling, high consistent curves are found in the measurements. For the samples with severe wrinkling but without structure rupture, curves for small VSGs do not converge after a certain longitudinal strain. For the Celgard 2325 TD, as the intermediate PE layer rupture occurs in the necking region, the curves for small VSGs applied on necking converge to a different path compare to the curves for other VSGs.

In the range of strain between 0 and 0.5, the out-of-plane Poisson's ratio can be regarded as zero and no thickness change can be found, while the in-plane Poisson's ratio varies with strain for all separators due to the meso-scale interactions of the pore structures. A polynomial function is used to describe the relationship between Poisson's ratio and longitudinal strain, and the coefficients are fitted by the DIC results. Distinct variations of Poisson's ratios are found in different samples, i.e. relatively small variations of Poisson's ratio (remained below 0.4) are found in dry-processed separators, while Poisson's ratios of wet-processed separators increase considerably and even exceed unity for the one with

thickness of 16 μm . The porosity variations associated with strains are calculated by the deformation based on the assumption of constant volume of the matrix material. Different relationships between porosity and strain are found, in which the porosities of dry-processed separators increase with strain while the porosities of wet-processed separators decrease with strain. These characterisations also have a good agreement with the previous work [38] and SEM images of the microstructures of the samples, which demonstrates that the proposed porosity equation is reliable and can be used in both mechanical analyses and coupled mechanical-electrochemical analyses for batteries.

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Appendix A.

A1. Details of thickness measuring

In order to eliminate the measurement errors caused by the speckle patterns on the surface and the curling at the edges, a supplementary uniaxial tensile test was carried out for the thickness measurement. The sample size here was determined to be a 160 mm $\times$ 25 mm strip and the starting grip separation was set as 100 mm. All supplementary tests were conducted following the method described in Section 2.2, but they were stopped when the crosshead displacement reached 100mm. A digital micrometre with high precision of 1 μm was used by following the TAPPI T411 method. The measurement was stopped by the top ratchet when the contact force reaches 5-10 N to ensure the accuracy of the measurement. All samples were measured before and after the tensile test and the measurements were repeated 5 times for each specimen. The measuring results are summarised in Table A1.

Table A1

The thickness values of separator samples.

Sample	Direction	Thickness (μm)	
		Before test	After test
Celgard 2325	MD	25 $\pm$ 1	25 $\pm$ 1
	TD		18 $\pm$ 1 in the necking region and 25 $\pm$ 1 in other regions
Celgard 2500	MD	25 $\pm$ 1	25 $\pm$ 1
	TD		25 $\pm$ 1

Hipore-16	MD	16±1	16±1
	TD		16±1
Hipore-25	MD	25±1	25±2
	TD		25±2

A2. Other supplementary experimental figures

Fig. A1 shows the uniaxial tensile engineering stress-strain curves with error bars (determined by standard deviation) for all samples.

Fig. A1 Engineering stress-strain curves of (a) Celgard separators in MD, (b) Celgard separators in TD, (c) Hipore-16 and (d) Hipore-25.

Fig. A2 and A3 shows the homogeneous strain distributions for dry-processed Celgard separators in MD and wet-processed Hipore separators in both directions.

Fig. A2 Full-field longitudinal strains of (a) Celgard 2500 MD, (b) Hipore-16 MD, (c) Hipore-16 TD, (d) Hipore-25 MD, and (e) Hipore-25 TD.

Fig. A3 Full-field transverse strains of (a) Celgard 2500 MD, (b) Hipore-16 MD, (c) Hipore-25 MD, and (d) Hipore-25 TD.

Fig. A4 shows the consistent transverse strain vs. longitudinal strain curves of samples without wrinkling and structure rupture.

Fig. A4 The transverse strain vs. longitudinal strain curves with different VSG for (a) Celgard 2500 MD, (b) Hipore-16 MD, (c) Hipore-25 MD , and (d) Hipore-25 TD.

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