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Temperature and strain rate dependent behavior of polymer separator for Li-ion batteries[☆]

Sergiy Kalnaus[a,*], Yanli Wang[b], Jianlin Li[c], Abhishek Kumar[a], John A. Turner[a]

[a] Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6164, USA
[b] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6164, USA
[c] Energy and Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6164, USA

HIGHLIGHTS

- Anisotropic mechanical behavior of triple-layer separator studied in detail.
- Strain rate and temperature effects investigated.
- Thermal effect was found anisotropic and pronounced in transverse direction.

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ABSTRACT

Safe performance of advanced Li-ion batteries relies on integrity of the separator membrane which prevents contact between electrodes of opposite polarity. Current work provides detailed study of mechanical behavior of such membrane. Temperature and strain rate sensitivity of the triple-layer polypropylene (PP)/polyethylene (PE)/polypropylene (PP) porous separator for Li-ion batteries was studied experimentally under controlled temperatures of up to 120° (393 K), and strain rates (from $1 \cdot 10^{-4}$ s^{-1} to 0.1 s^{-1}). Digital image correlation was used to study strain localization in separator under load. The results show significant dependence of mechanical properties on temperature, with the yield stress decreasing by 30% and elastic modulus decreasing by a factor of two when the temperature is increased from 20 °C to 50 °C. The strain rate strengthening also decreased with higher temperatures while the temperature softening remained independent of the applied strain rate. Application of temperature creates long lasting changes in mechanical behavior of separator as was revealed by performing experiments after the annealing. Such delayed effect of temperature application appears to have directional dependence. The results demonstrate complex behavior of polymer separator which needs to be considered in proper safety assessments of Li-ion batteries.

1. Introduction

Lithium-ion batteries have become a major rechargeable energy source in multitude of devices from consumer electronics to military applications and are the primary technology for electric vehicles (EVs). These are rather complicated systems combining components that have very different physical and mechanical properties. The overall principle is based on separating reduction and oxidation reactions in space and delivering Li ions to either electrode via electrolyte. While there have been significant developments in the area of all solid state batteries [1–4], these systems are currently limited to thin film cells and the vast majority of commercial batteries are based on liquid electrolytes. In this case the ionic current is delivered between the electrodes via liquid, which is a solution of lithium salt in organic solvents. The inherent safety concern in this case is the flammability of such electrolyte, which can be a source of catastrophic fire event of a battery, provided there is a source of high temperature and ignition. Apart from external events (overheating), the source of ignition can come from the rapid battery discharge due to internal short circuit. In order to prevent this, the spatial separation of

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* Corresponding author.
E-mail address: kalnauss@ornl.gov (S. Kalnaus).

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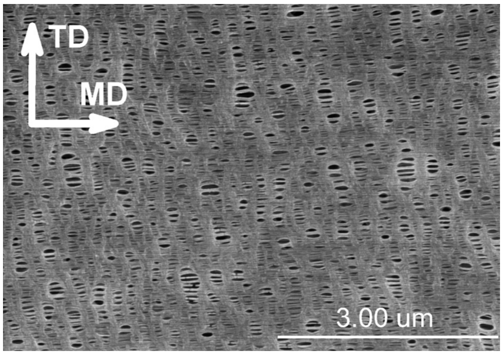

Fig. 1. Microstructure of Celgard 2325 separator.

electrodes in a liquid electrolyte battery is achieved by placing a porous non-conductive membrane between them. This membrane, termed separator should therefore satisfy several requirements: (i) it should have significant mechanical strength; (ii) it should be sufficiently porous to allow transport via liquid electrolyte; (iii) it should display low thermal shrinkage so that the edges of electrodes do not get exposed and do not come into contact. It therefore can be stated that separator is a critical safety component in a battery. The requirements of safety resulted in development of several standards describing integrity of separator. The manufacturing of Li-ion cells is automated by using winding machines where the long strip of separator is wound between the layers of electrodes of opposite polarity. Since the separator in this operation is under tension, the requirement for the tensile strength in winding direction was proposed as the minimum Young's modulus of 100 MPa [5]. It should be mentioned that in dry manufacturing of separators, the machine direction (MD) is much stronger than orthogonal transverse direction (TD) and for this reason the separator strips are cut so that the winding direction coincides with MD. The other assessment of separator integrity is done by conducting the puncture strength test (ASTM D4830) [6]. The current requirement for the separator is 300 g of critical puncture weight applied to a needle with 1 mm tip radius [7]. The above requirements were determined to be sufficient for a routine battery manufacturing and operation under normal conditions. In the event of external impact, such as in vehicle crash, however, large strains and stresses can develop and therefore the above standards cannot be an adequate guidance for separator strength. In addition, clear majority of separators are made of polymer materials and therefore are expected to change behavior as a function of temperature. In addition, some separators are manufactured as triple-layer membrane with the middle layer designed to melt at elevated temperatures and thus shut the transport of ions between the electrodes. This additional safety feature serves as a circuit breaker in the event of battery malfunction; however at the same time the mechanical strength of the separator can be expected to be different within the temperature range close to the melting temperature. It should be mentioned that there has been significant effort towards characterization of separators documented in published literature. In some occasions however the separator was removed from the disassembled battery and tested without specification of its nomenclature [8]. Otherwise, tensile mechanical behavior was investigated in [9–12] for polypropylene

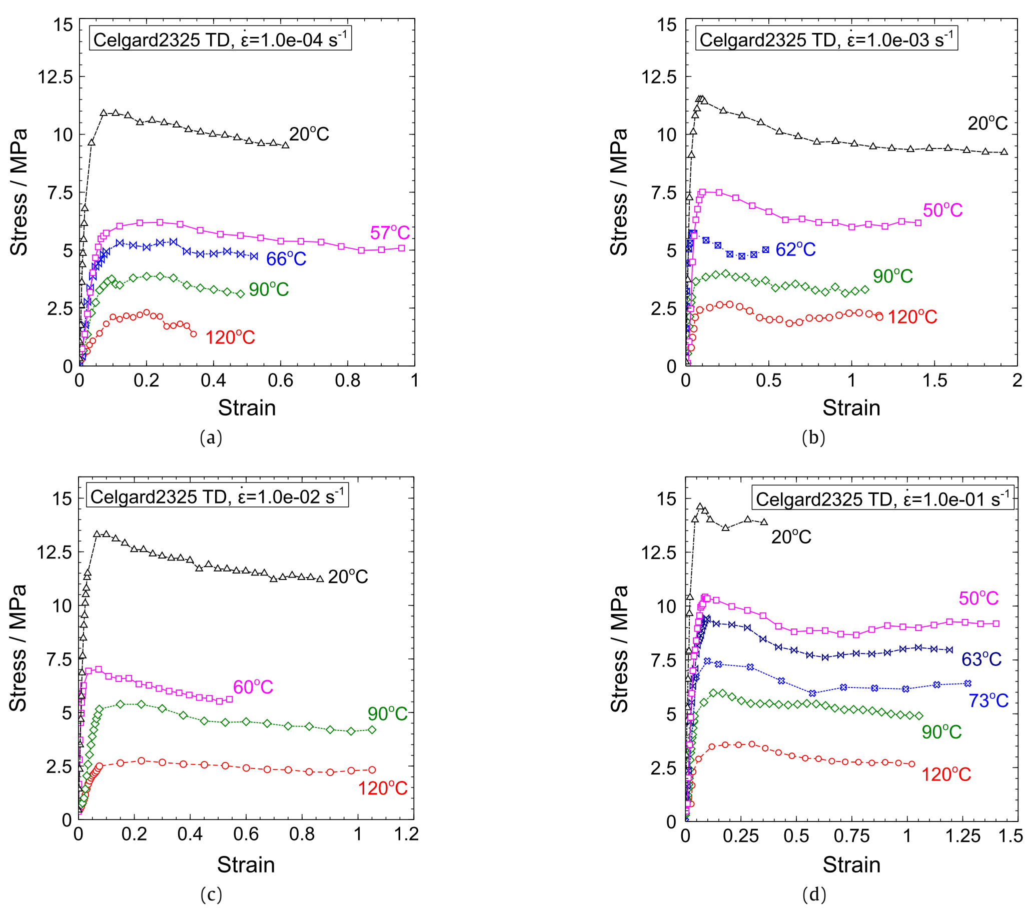

Fig. 2. Tensile behavior of separator in transverse direction (TD): (a) $\dot{\epsilon} = 1.0 \cdot 10^{-4}\ s^{-1}$; (b) $\dot{\epsilon} = 1.0 \cdot 10^{-3}\ s^{-1}$; (c) $\dot{\epsilon} = 1.0 \cdot 10^{-2}\ s^{-1}$; (d) $\dot{\epsilon} = 1.0 \cdot 10^{-1}\ s^{-1}$.