Failure Mechanisms in Battery Separator Materials

D. Zheng,[1] D.W. Schaefer,[1] R. Pekala[2]
[1]Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH, U.S.A.
[2]Entec Membranes LLC, Lebanon, OR, U.S.A.

Introduction

Porous polymer membranes play an important role in the thermal response of Li ion batteries. Porous 25-μm-thick polyolefin sheets separate the anode and cathode to prevent shorting of the electrodes. These membranes are porous to allow conduction of ions necessary to complete the electrochemical cell.

The thermal response of this membrane is critical to battery safety. During a thermal excursion above 120°C, the separator is designed to densify by pore collapse so ionic current ceases. If, on the other hand, a hole should develop in the membrane, the electrodes would short circuit, leading to a runaway thermal reaction and possible explosion. Which scenario develops is known to depend on the composition and processing of the separator material. Undoubtedly, shutdown also depends on the pore morphology. Indeed, it is likely that the morphology of the pores is the critical factor that controls the failure mode and that this morphology is controlled by the composition and processing of the film.

The purpose of this work is to understand pore evolution in order to improve the materials performance of these separators. The project seeks to (1) characterize the evolution of pore structure during thermal excursions, (2) elucidate the mechanism underlying this evolution, and (3) use this information to improve the composition and processing of membrane separators.

Currently, there is no good way to examine porosity during the failure scenario. Indirect information can be extracted from gas flow measurements on the extracted membrane materials, but the data are difficult to relate to actual pore structure. In addition, gas flow is impossible in realistic experiments performed in the presence of an electrolyte. Ultrasmall-angle x-ray scattering (USAXS) not only allows quantitative characterization of pore morphology but can also be used to examine the evolution of pore morphology in real time during thermal aging. Major changes in transport characteristics occur between 125 and 130°C.

Methods and Materials

Porous membrane separators were provided by Entek Membranes LLC. We studied two types of membranes, Asahi and Teklon, which are made by different manufacturers and differ in their thermal response characteristics. Figure 1 is a scanning election microscope (SEM) image of the Asahi sample. It is believed that both membranes are manufactured from high-density polyethylene. These membranes were heated up to 150°C in air and in the presence of ethylene carbonate (EC) and EMI fluid, a complex ionic liquid of proprietary origin.

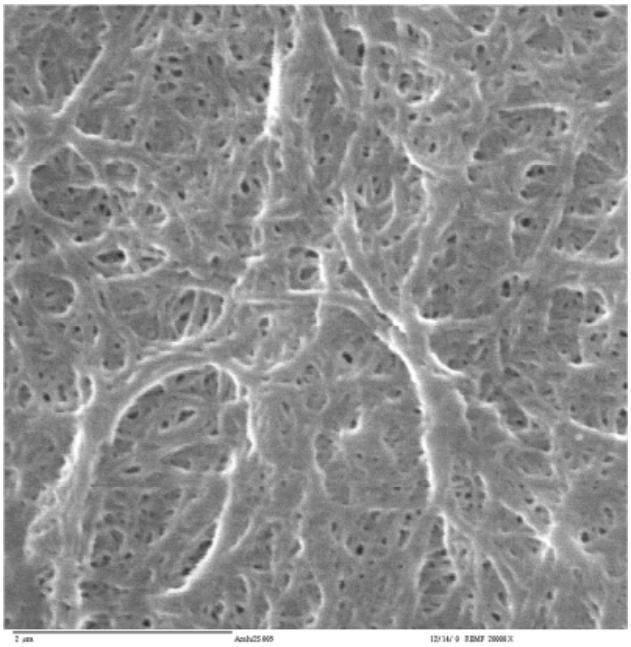

FIG. 1. SEM image of Asahi membrane battery separator surface. USAXS indicates the porosity is on the scale of 0.14 μm in diameter. The bar at the lower left is 2 μm.

The samples were studied in both single- and double-bounce geometry. In the former, results for all orientations are averaged, so all pore anisotropy information was lost. Desmearing was necessary to extract the angularly averaged scattering function.

For the double-bounce geometry, two types of scans were made: USAXS and aniso. USAXS scans were done with a particular sample orientation corresponding to the azimuthal angle, which was measured with respect to the machine direction or film draw direction. For aniso scans, the analyzer crystals were set to a particular value of momentum transfer q, and the sample was rotated to yield a plot of the intensity versus azimuthal angle.

Results and Discussion

Figures 2 and 3 are conventional azimuthally averaged USAXS scans as a function of temperature for the two

samples, Asahi and Teklon. We take the inflection in the curve to be the mean pore size. The data are fit by using the UNI-CAT unified fitting procedures to yield radii of gyration of 701 Å for the Asahi sample and 1400 Å for the Teklon sample in the low-temperature state.

Both samples were studied after exposure to temperatures as high as 150°C in the presence of EC. The films were exposed for 30 minutes, cooled, dried, and studied in the dry state at room temperature. These data are reported as a function of temperature in Figs. 2 and 3. These data show that there is no change of the porosity up to 135°C for the Teklon sample, whereas there is considerable evolution of the Ashi sample at 135°C. In addition, both samples showed the emergence of crystallinity, as evidenced by the long-period peak near 0.02 $Å^{-1}$ that is typical of semicrystalline polymers. From the position of the peak, we can conclude that the long period is longer for Teklon than for Asahi.

Side-bounce experiments showed that both samples have quite anisotropic pores. Anisotropy results from the pore formation process itself. Porosity is induced by either a uniaxial or a biaxial drawing of the films.

Figure 4 shows the aniso scans as a function of temperature for the Asahi sample at q = 0.001 $Å^{-1}$. The data show a more continuous evolution of the pore anisotropy as a function of temperature than would be expected based on Fig. 2.

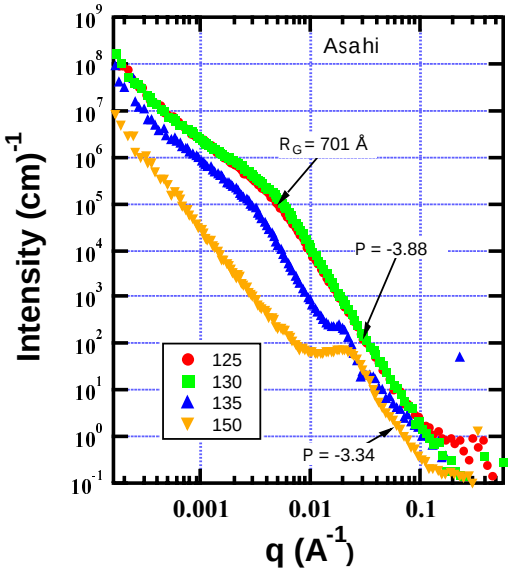

FIG. 2. Desmeared azimuthally averaged USAXS scans for the Asahi membrane as a function of conditioning temperature. P is the power-law exponent. R_G is the radius of gyration from level 1 of a three-level unified fit. Films were conditioned in the presence of EC for 30 minutes at each temperature, dried, and studied at room temperature.

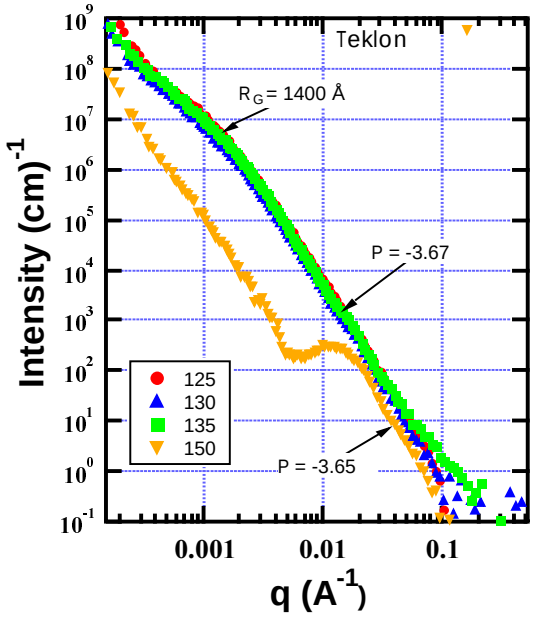

FIG. 3. Desmeared azimuthally averaged USAXS scans for Teklon as a function of EC conditioning temperature.

The anisotropy of the samples can be quantified using the Hermans orientation function. Figure 5 shows the evolution of the Hermans function as a function of conditioning temperature. These samples were conditioned in air for 30 minutes, cooled, and studied at room temperature.

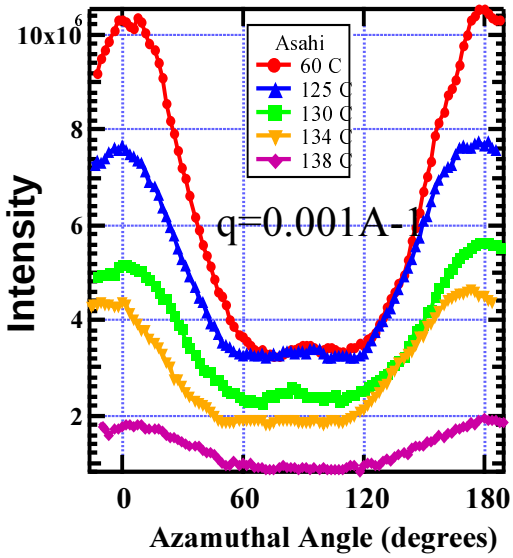

FIG. 4. Aniso scan of the Asahi sample at q = 0.001 $Å^{-1}$. These samples were conditioned at the temperatures indicated in the dry state, then cooled to room temperature for USAXS analysis.

The evolution of the pore anisotropy depends on q, as shown in Fig. 5 for the Asahi material. At q = 0.001 Å^{-1}, we were measuring anisotropy on length scales larger than the pore radius, whereas at 0.0076 Å^{-1} we were measuring anisotropy on lengths comparable to the pore radius. It appears that the pores become more anisotropic (0.0076 Å^{-1}), whereas correlations between the pores (q = 0.001 Å^{-1}) become less anisotropic as the pores collapse.

Acknowledgments

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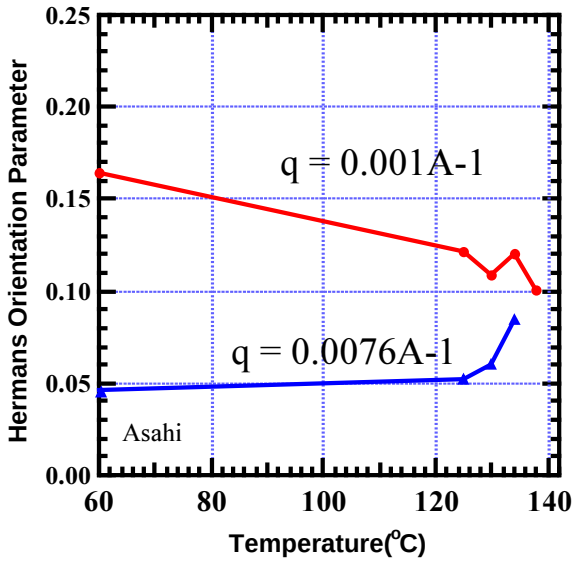

FIG. 5. Evolution of the Hermans orientation function for the Asahi sample as a function of conditioning temperature. From the q = 0.0076 Å^{-1} results, we conclude that the pores are oriented in the machine direction and that the anisotropy increases with conditioning temperature.