

Study of Polypropylene Separator Degradation in High-Power Lithium –Ion Cells

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Under the Department of Energy's Advanced Technology Development program, high-power lithium-ion batteries are stored, cycled, and/or abused and then assessed *via* a host of characterization and diagnostic tests [1]. We have examined Celgard® 2300 membranes from several of these batteries in order to determine their role in the power loss that occurs when these cells are tested at elevated temperatures.

Membrane impedance has received limited consideration in the literature and has largely been overlooked in battery diagnostic work. The few studies that have demonstrated membrane impedance rise upon exposure to high temperatures have not identified the source of this increased resistivity [2,3]. Other studies showing that porosity is a determining factor in membrane ionic conductivity have treated porosity as a static characteristic of the membrane and have not investigated what might cause its changes [4-6].

Five samples of Celgard® 2300 membranes were studied: fresh material, membrane from a new battery that had undergone characterization tests but no cycling (Cell A), a membrane from a battery that had been cycled at 45°C for 4 weeks (10% power loss, Cell B), and membranes from batteries that had been stored at 55°C for 8 weeks (14% power loss, Cell C) and 28 weeks (24% power loss, Cell D).

Impedance measurements of these membranes reveal that membrane ionic resistivity increases significantly with cell power loss (Fig. 1). It is quite clear that both cell cycling and aging, as well as the temperature at which the cell was tested, had a significant impact on the cell power loss and the membrane impedance rise. We also observed that membrane impedance varied significantly at different locations, especially for the membranes that were tested at elevated temperatures. This variance is represented by the large error bars for the membranes from cells C and D.

Atomic Force Microscopy (AFM) images of the separators reveal dramatic changes in the membrane surface morphology. The regular network of polypropylene fibers that constitute the fresh membrane become swollen and disrupted by deep cracks and grain imprints. This is particularly well visible in the membranes removed from the cells that had been stored at 55°C. Furthermore, images of the membrane from cell D revealed foreign particles lodged between polypropylene fibers at the membrane surface. Raman microscopy spectra of these inclusions indicated that they were cathode active material ($\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) and acetylene black, which also originated from the cathode. Both the swelling of fibers and the blocking of membrane pores by loose particles from the cathode decrease membrane porosity, thereby increasing both the ionic mean free path across the membrane and the membrane impedance. The cracks in the fiber structure and the accretion of foreign particles from the cathode decrease the uniformity of the membrane surface, resulting in the

greater variation of membrane impedance in membranes C and D as compared to the other membranes.

We determined that the membrane impedance increase which accompanies cycling and/or aging of high-power Li-ion cells accounts for nearly 15% of the total cell impedance rise.

The results of a model experiment, which was carried out to investigate the mechanism of membrane degradation in 1.0 M LiPF_6 , EC-EMC (1:1 by volume) will also be discussed.

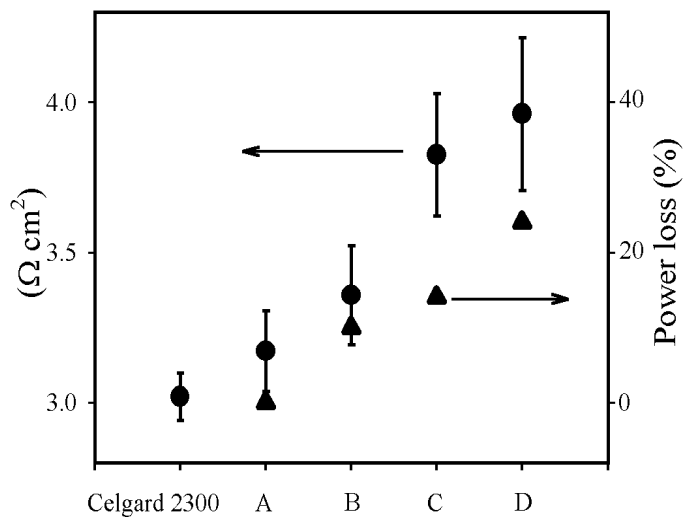


Figure 1: Membrane area-specific impedance (circles, left-hand ordinate) and cell power loss (triangles, right-hand ordinate). Note the dramatic rise in impedance between membranes B (cell cycled at 45°C) and membrane C (cell stored at 55°C) and the large error bars associated with membranes C and D.

References

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