Procedure for Determining Shutdown Temperature of Battery Separators

Background

Laman et al. [1] were the first to determine the electrical impedance of battery separators as a function of temperature (from 25-200^{o}C at a scan rate of 1^{o}C/min). They found the impedance increased by several orders of magnitude near the melting point of the separator, but then rapidly dropped to near zero. By stacking layers of polyethylene and polypropylene membranes together they were able to maintain a high impedance over the temperature range corresponding to the melting points of polyethylene (135^{o}C) and polypropylene (165^{o}C). These results were verified by Geiger et al. [2] using steady-state measurements in a thermally-stable electrolyte. Spotnitz et al. [3] extended the procedure of Laman et al. [1] to allow faster scan rates (~60^{o}C/min) using the thermally-stable electrolyte of Geiger et al. [2].

Materials Required

1) RLC meter with digital output to data acquisition system. The RLC bridge should be capable of providing impedance values to the data acquisition system at a rate of at least 10 per minute.
2) Data acquisition system (for example, LabView) for recording temperature and impedance.
3) Heated press (example, Carver with high-power heaters) and temperature controller (example, Eurotherm equipped for RTDs). Optionally, a insertable cooling means for the press can be used to allow for faster turnaround between tests.
4) Cell (see attachment)
5) Electrolyte – 1 M lithium trifluoromethanesulfonimide (HQ-115, 3M Co.) in a 1:1 by volume solution of propylene carbonate and triethylene glycol dimethyl ether. The electrolyte should be stored in a drybox.
6) Two fast response, micro RTDs.

Experimental

Figure 1 shows a schematic of the experimental arrangement. The experiment should be carried out in a fume hood. Two RTD temperature sensors are included in the test cell. The temperature controller uses one of the RTDs while the other is used as a check. The readings from both RTDs should be recorded by the data acquisition system, as well as the output from the RLC meter.

The procedure for carrying out the test is as follows.

1) Place a few drops of electrolyte onto the separator to saturate it, and place the separator into the test cell.

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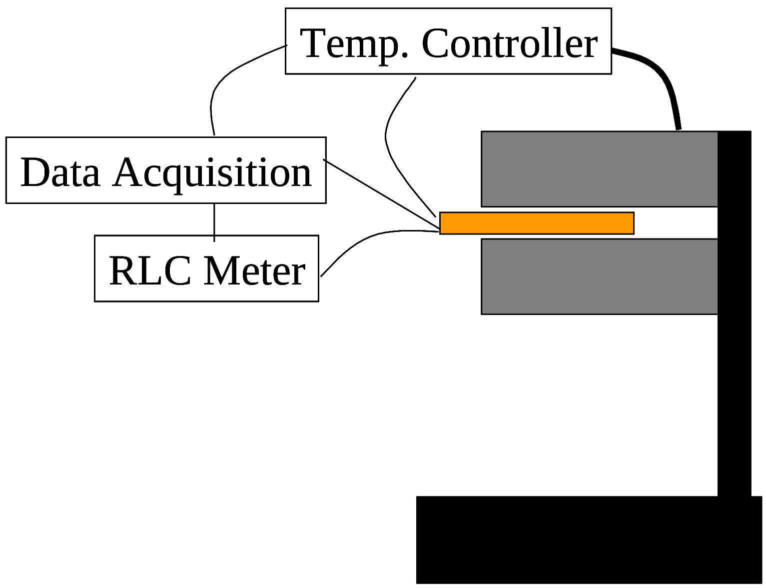
2) Make sure that the heated press is below 50°C, and if so, place the test cell between the platens and compress the platens slightly so that only a light pressure is applied to the test cell (<50 lbs for a Carver "C" press).
3) Connect the test cell to the RLC bridge and begin recording temperature and resistance. When a stable baseline is attained, then start ramping the temperature of the press at 10°C/min using the temperature controller.
4) Turn off the heated platens when the maximum temperature is reached or when the separator impedance drops to a low value.
5) Open the platens and remove the test cell. Allow test cell to cool. Remove separator and dispose of.

Figure 1 Experimental Arrangement for Shutdown Temperature Test.



Results

The results should be reported graphically on semi-log paper plotting the log of the impedance (ohm-cm^2) versus temperature (°C). The temperature value reported should be the average of the two RTD readings.

Normally, the impedance will increase from its initial value to some maximum value, stay at that maximum value over a limited temperature range, and then decrease to a value lower than the initial value. Shutdown occurs if the impedance maximum is at least 100X greater than the initial impedance value. Somewhat arbitrarily, the shutdown temperature, T_{SD} (°C), is defined as the temperature at which the impedance first rises to 100X its initial value. The temperature at which the impedance first drops to 100X its initial value is defined as the melt integrity temperature, T_{MI} (°C). The shutdown window is defined as the difference between these two temperatures (=T_{SD}-T_{MI}).

References:

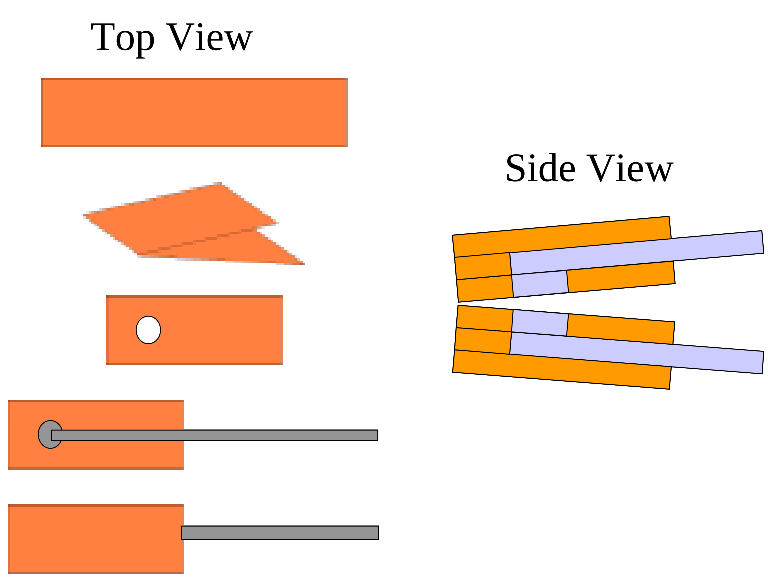
[1] F. C. Laman, M. A. Gee, J. Denovan, "Impedance Studies for Separators in Rechargeable Lithium Batteries", J. Electrochem. Soc., Vol. 140 No. 4, April 1993 p. L51-L53.
[2] P. Geiger, R. Callahan, C. Dwiggins, H. Fisher, D. Hoffman, W.-C. Yu, K. Abraham, M. Jillson, T. Nguyen, "Advanced Separators for Lithium Batteries", The 11th Intl. Sem. Primary & Secondary Battery Technology and Applications, 1994.
[3] R. Spotnitz, M. Ferebee, R. Callahan, K. Nguyen, W.-C. Yu, M. Geiger, C. Dwiggins, H. Fisher, D. Hoffman, "Shutdown Battery Separators", The 12th Intl. Sem. Primary & Secondary Battery Technology and Applications, 1995.

Attachment Design and Construction of Test Cell

The test cell can be constructed from commercially available materials (Kapton film and tape, nickel foil, steel plates,).

Cut out a piece of Kapton film (2 mil thick) 3 inches wide by 8 inches long. Fold the film about the midpoint of the length so two layers of film result that are each 4 inches long. Punch a ¼" hole in through both layers of film approximately 2" away from the fold and centered about the width. Also punch out two ¼" diameter disks from a 2 mil nickel foil and spot weld onto the nickel foils leads consisting of nickel foil (1/8" wide 8" long). Force each nickel disk into the holes in the Kapton from outside of the bend (see Figure A1). Insulate the exposed nickel using Kapton tape. Figure A1 summarizes this process. The bend in the Kapton film serves as a hinge to open the layers and allow the separator to be inserted between the two nickel electrodes.

Figure A1 Construction of test cell. Not to scale.



The cell should be placed in a fixture consisting of two steel plates (1/8" thick, 5" wide, 6" long). In one of the plates, grooves should be made to place the RTDs.

Figure A2 Bottom steel plate to hold test cell and RTDs. Not to scale.