Journal of Power Sources 262 (2014) 93–103

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

The five modes of heat generation in a Li-ion cell under discharge

Rengaswamy Srinivasan*, A. Carson Baisden, Bliss G. Carkhuff, Michael H. Butler

Applied Physics Laboratory, The Johns Hopkins University, Laurel, MD 20723-6099, United States

HIGHLIGHTS

- Li-ion cell under discharge generates thermal energy through five different modes.
- Three of the five modes are the electrolyte, anode, and cathode resistances.
- Two of the five modes are the entropy change in the cathode and the anode.
- The five are dependent on the rate of discharge and the environmental temperature.
- Measurement and quantification of heat generated by each mode is demonstrated.

ARTICLE INFO

Article history:
Received 5 December 2013
Received in revised form
14 March 2014
Accepted 17 March 2014
Available online 27 March 2014

Keywords:
Li-ion cell
In situ tracking of thermal runaway
Noninvasive sensors
Resistive heating
Entropy-generated heating

ABSTRACT

A lithium-ion cell under discharge generates thermal energy (Q) through five different internal parameters or modes: the electrolyte resistance (R_s), anode resistance (R_a), cathode resistance (R_c), and entropy changes in the cathode (ΔS_c), and the anode (ΔS_a). This work demonstrates a set of tools to measure/quantify the heat generated by each parameter separately during discharge. These five sources are not dependent upon each other; they are dependent on the state of charge and the environmental temperature (T_{env}). The Q generated by each mode varies with degree of discharge and T_{env}. R_s generates most of the Q in the −10 °C to 40 °C range; R_c becomes significant at T_{env} <20 °C. Constant current discharge does not cause a monotonic increase in anode and cathode temperatures (T_a and T_c), due to the direction of change in ΔS_c and ΔS_a. Negative change in ΔS_a for the carbon anode cools it, causing the T_a to level off and even decrease with increased discharge. ΔS_c for lithium manganese oxide cathode is positive at some SoC and negative at others, preventing a monotonic increase in T_c. Measuring the five Qs separately opens the opportunity to study thermal-runaway from the perspective of the anode, cathode and electrolyte.

1. Introduction

Lithium-ion cells are among the optimal electrical energy storage and power delivery devices. During each charge–discharge cycle, the cell converts electrical energy into chemical and thermal energies; the cell is only capable of storing the chemical energy. The discharge reverses the process, converting the chemical energy into electrical and thermal energies. The thermal energy generated by the cell during charging and discharging is permanently lost, never stored or recovered as electrical or chemical energies, and accounts for the energy loss experienced during every charge–discharge cycle. Thermal energy generated inside the cell increases the internal temperature of the cell and under extreme conditions can initiate other exothermic chemical reactions causing the cell to vent, and sometimes transitioning the cell to a thermal runaway condition. Venting and thermal runaway are major safety issues related to Li-ion cells, and their causes and ramifications can be found in recent reviews and news articles [1,23].

The most common and accepted modes of thermal energy (Q) generation during charging and discharging of Li-ion cells are entropy- and internal resistance-related, and researchers use indirect measurements and thermal models to estimate the magnitude of Q [4–6]. The more direct measurements of Q are made using calorimeters [7–9]. However, such measurements only yield the sum of all the heats, not the individual components of the heat generated inside the cell.

It has been commonly recognized that the heat is generated through five different modes by five independent components inside the cell [5–7]. They are: i) the electrolyte resistance (R_s);

* Corresponding author. Tel.: +1 443 778 6378; fax: +1 443 778 5937.
E-mail addresses: Rengaswamy.srinivasan@jhuapl.edu, srinir@comcast.net (R. Srinivasan).

http://dx.doi.org/10.1016/j.jpowsour.2014.03.062
0378-7753/

ii) the anode resistance (R_a); iii) the cathode resistance (R_c); iv) the entropy change in the cathode (ΔS_c); and v) the entropy change in the anode (ΔS_a). The rate of heat generated by each one of these five modes is dependent upon the temperature of the cell, and the amplitude and direction of the current. The ability to measure the individual contribution by each mode to Q, especially during the course of charging and discharging, yields invaluable information about the thermal behavior of each mode. It is, perhaps, the most successful way to track all the vital points inside the cell, and provide a trajectory for any impending errant behavior by the cell.

The major focus of the work described below is to quantify the contributions by the individual modes to the thermal energy outputted during discharge, and to reconcile those individual contributions with the overall thermal behavior of the cell during discharge. In addition, the work also demonstrates: i) the instantaneity of the impact of the changes in the discharge current on T_a and T_c; ii) ultraslow responses of the surface temperature (T_{surf}) to the changes in the current; and iii) inhomogeneity in the temperature within the cell, namely, differences between the T_a and T_c during discharge; and iv) presence of correlation between T_a and T_c with T_{env}, and absence of correlation between the T_{surf} and T_{env}.

1.1. Highlights of the techniques used in online monitoring of heat generation

Two different techniques are available to estimate the heat energy generated by each of the five modes. For estimating the entropy-related thermal energy, we used a recently-acquired technique that allows one to measure T_a and T_c in situ, while the cell is under charge and discharge [10]. By measuring, for example, T_c, one could compute $Q_{\Delta S_c}$, the heat associated with the entropy change in the cathode (ΔS_c); similarly, $Q_{\Delta S_a}$ by measuring T_a. On the other hand, for estimating the Joule heating, one would need the R_a, R_c, and R_s values measured during discharge.

The R_a, R_c, and R_s values can be obtained using conventional electrochemical impedance spectroscopy (EIS). The technique to measure T_a and T_c is also based on impedance. A measure of the phase shift (ϕ) between an applied voltage (or current) and the resultant current (or voltage) at a single frequency is a function of

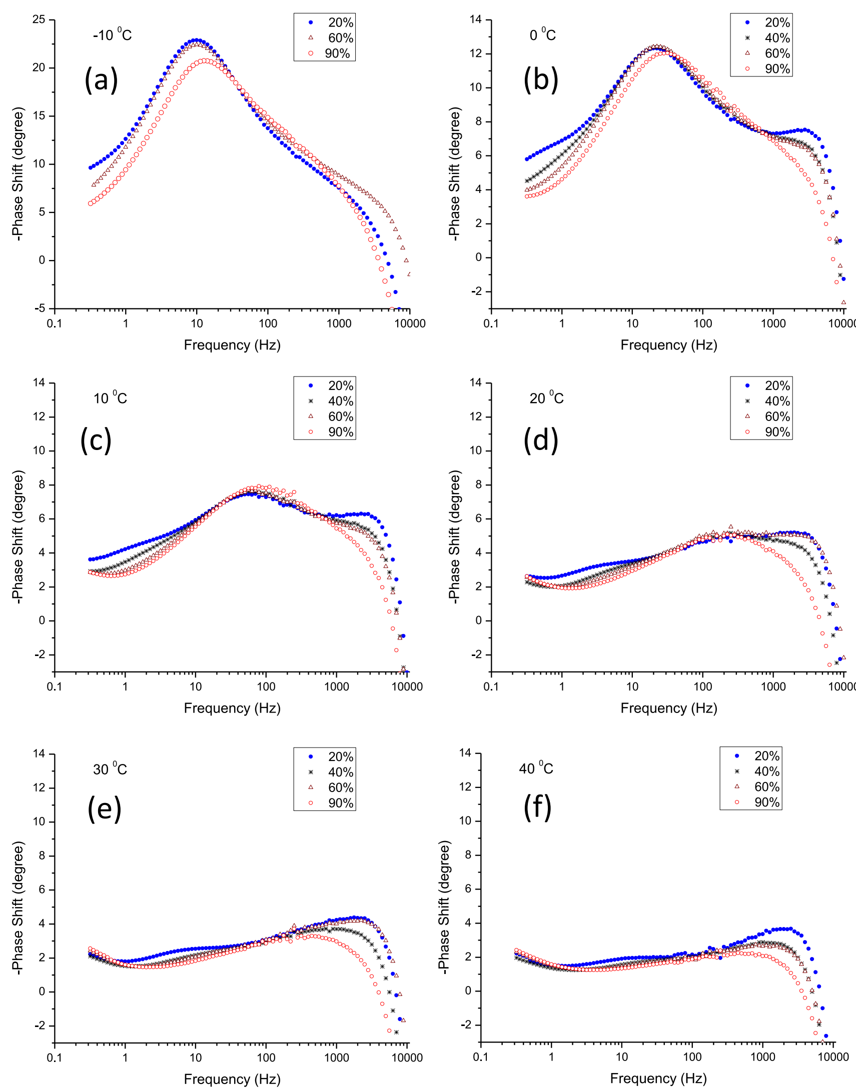

Fig. 1. Bode plots showing phase shift, ϕ, versus frequency for a 4.4-Ah Swing 4400 Li-ion cell at different SoC in six different T_{env} from −10 °C to 40 °C as indicated in (a)–(f). The value of ϕ at 20 Hz represents the T_c, and at 100 Hz represents T_a. Note that at all frequencies between 20 Hz and 200 Hz, ϕ is insensitive to SoC and sensitive to T_{env}. The associations of the values of ϕ to T_c at 20 Hz and to T_a at 100 Hz are explained in Fig. 4.