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Heat loss distribution: Impedance and thermal loss analyses in $LiFePO_4$/graphite 18650 electrochemical cell

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HIGHLIGHTS

- Determination of entropic coefficient and its correlation with cell temperature.
- Contribution of reversible and irreversible heat losses at various current rates.
- Compliance of total heat loss by ARC with sum of component heat losses.
- Resolving internal resistance into different components using impedance technique.
- Ohmic resistance is found to be the major contribution to internal resistance.

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ABSTRACT

We report here thermal behaviour and various components of heat loss of 18650-type $LiFePO_4$/graphite cell at different testing conditions. In this regard, the total heat generated during charging and discharging processes at various current rates (C) has been quantified in an Accelerating Rate Calorimeter experiment. Irreversible heat generation, which depends on applied current and internal cell resistance, is measured under corresponding charge/discharge conditions using intermittent pulse techniques. On the other hand, reversible heat generation which depends on entropy changes of the electrode materials during the cell reaction is measured from the determination of entropic coefficient at various states of charge/discharge. The contributions of irreversible and reversible heat generation to the total heat generation at both high and low current rates are evaluated. At every state of charge/discharge, the nature of the cell reaction is found to be either exothermic or endothermic which is especially evident at low C rates. In addition, electrochemical impedance spectroscopy measurements are performed on above 18650 cells at various states of charge to determine the components of internal resistance. The findings from the impedance and thermal loss analysis are helpful for understanding the favourable states of charge/discharge for battery operation, and designing better thermal management systems.

1. Introduction

In 1991, Sony and Asahi Kasei [1] introduced the first rechargeable lithium-ion batteries (LIBs) which use layered $LiCoO_2$ (LCO) as cathode and graphite as anode. Such LIBs have been outperforming other secondary batteries such as NiCd, NiMH and lead acid batteries. Until the introduction of lithium iron phosphate ($LiFePO_4$) and other phospho-olivines in 1996 by Padhi et al. [2], the layered LCO dominated the commercial battery market in its use as the positive electrode material with high energy density [3]. However, it suffers from serious drawbacks such as high cost, low capacity, toxicity, oxygen evolution at over charge and thermal runaway issues [4,5]. The impending need for improved thermal management paved the way for the introduction of new derivative positive electrode materials by substituting Co either partially or fully with other metals such as Ni, Mn, Al, Mg, Cr, etc. [6]. However, most of the oxide-based cathode materials such as layered $LiNi_{1-x-y}Co_xMn_yO_2$ ($0 \leq x$ & $y \leq 1$) and spinel $LiMn_2O_4$ exhibit disadvantages such as irreversible phase transformations and John-Teller distortion [4]. Recently, $LiFePO_4$ (LFP) has proved its superiority by its good cycling behaviour, high theoretical capacity and

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thermal stability in comparison with established cathode materials such as $LiCoO_2$ and $LiMn_2O_4$ [7]. Also, LFP is found to have no oxygen release at higher temperature or voltage which triggers thermal runaway of the cell [8,9].

Saito et al. [10] performed calorimetric experiments on LIBs with $LiCoO_2$ as cathode material and demonstrated different criteria such as electrochemical polarization, internal resistance and battery reaction for heat losses during charge and discharge. Selman et al. [11] reported exothermic and endothermic nature of heat losses in commercial LIBs using electrochemical calorimetric measurements. Viswanathan et al. [12] studied the effect of entropy change as well as heat generation at different C rates for various cathodes and anodes in different commercial batteries. Ben Mayza et al. [13] reported total heat generation in 18650-type $LiFePO_4$/graphite using ARC at low current rates and estimated thermal runaway temperature for the same cell. Song et al. [14] studied the heat effects of $LiFePO_4$ coin cell and commented on the exothermic/endothermic phenomenon during the charge/discharge processes. Nieto et al. [15] developed a thermal model which describes the heat generation behaviour of Li-ion pouch cell at different current rates based on the calculation of heat generation from experimental measurements of internal resistance and entropic coefficient.

Although thermal studies are reported for $LiFePO_4$/graphite [16,17], the quantification of thermal losses and its components such as irreversible and reversible heat losses at different current rates are not reported in detail. In this study, the reversible heat loss accounting for the entropy generation during lithium intercalation/de-intercalation as well as the irreversible heat losses arising from the cell resistances are quantified for an 18650-type $LiFePO_4$/graphite cell. Such information is relevant for understanding the causes of thermal runaway in lithium-ion cells and provides valuable experimental data for electrochemical and thermal modelling of lithium-ion batteries [18–23].

2. Experimental

2.1. Accelerating rate calorimetry

The rate of heat generated (Q) in 18650 type lithium-ion batteries is measured by Accelerating Rate Calorimetry (ARC) with the control volume around the battery such that [13]

$$Q = MC_p\frac{dT}{dt} + hA\left(T_{surf} - T_{sink}\right) \tag{1}$$

where M (kg) is the mass of the battery, C_p (J.kg^{-1} K^{-1}) is the specific heat capacity of the battery, $\frac{dT}{dt}$ (K.s^{-1}) is the change in battery temperature with respect to time, hA (WK^{-1}) is the calorimeter constant, T_{surf} (K) is the surface temperature of the battery, and T_{sink} (K) is the temperature of the thermal sink surrounding the battery.

The ARC (Thermal Hazard Technology, Model: ES ARCSYS-001) was used to determine the total heat generation in the battery (Fig. 1a and b). According to the manufacturer, it has a precision of 0.2% and an accuracy of 0.7% in maintaining the adiabatic conditions inside the calorimeter. The ARC method determines the amount of heat expelled from the battery to the surroundings and heat generation rate of the battery by measuring the rise in battery temperature over time. The radiant heater inside the calorimeter heats up such that the thermal sink surrounding the battery follows closely the temperature of the battery during cycling in order to attain thermal equilibrium so that no heat is expelled from the battery to the sink. Now Equation (1) becomes

$$Q = MC_p\frac{dT}{dt} \tag{2}$$

The mass of the battery (M) is measured on an electronic balance while the C_p value is estimated by running a specific heat capacity test in ARC. The values of derivative $\frac{dT}{dt}$ are recorded at constant time intervals during the charge/discharge processes.

2.1.1. Determination of specific heat capacity (C_p)

For determination of specific heat capacity (C_p), a sample is prepared by wrapping three batteries of the same 18650-type cells together using an aluminium tape in a triangular configuration with a flexible Kapton heater placed between them as shown in Fig. 1d and e. This configuration ensures that the heat supplied by the heater is absorbed almost completely by the batteries. The power is supplied to the heater externally by a DC source. The maximum current and voltage applied across the heater can be limited externally. However, the specific heat capacity of the battery is independent of the power supplied across the heater. The sample is placed inside the calorimetric cavity with a K type thermocouple kept on its surface. The maximum error permitted for this type of thermocouple, in accordance with IEC 60 584–2:1995, is 1.5 °C between −40 and 375 °C. The specific heat capacity test can be used to determine the C_p values over the operating temperature range of a particular battery. A polynomial equation is generated by the ARC-ES software correlating the specific heat capacity and the temperature. However, a weighted average of the C_p values over the operating temperature range is determined and substituted to estimate Q in Equation (2). Although the C_p values increased with increase in temperature, the variation was lower than 5% in the whole temperature range. In this work, the C_p value was determined to be 0.94 ± 0.01 J.g^{-1} K^{-1}. This value will be used later for the determination of total heat loss from the cells.

2.1.2. Measurement of total heat generation

An in-house 18650-type $LiFePO_4$/graphite battery is fitted inside the calorimetric cavity as shown in Fig. 1c to estimate the heat generation under different current (C) rates. The battery is cycled at 1C, 2C and 5C rates using MACCOR battery tester to determine the total heat generated under both charge and discharge processes. The accuracy of the current and voltage measurements in MACCOR is 0.02% in the range of 0–20 A and 0–80 V respectively. The operating temperature has been set at 35 °C in the calorimetric cavity since it was reported that the heat generation for this specific battery is not influenced by the operation over the temperature range 35–55 °C [24].

2.2. Determination of internal resistance

The internal resistance (R_{in}) in a cell is a function of cell temperature and SOC/DOD since it depends on the levels of the thermal and chemical equilibriums [25]. In this study, the internal resistance is determined using intermittent pulse technique where charge/discharge current pulses were applied while the voltage response was recorded using Arbin battery tester (Model BT2000, USA) in order to determine the total overpotential resistance as a function of SOC/DOD and the cell temperature. The accuracy of measurement in Arbin tester is 0.02% in the voltage range −2 to 10 V and current range 0–10 A.

During charge/discharge process, a pulse of 7 A current (5C, where 1C refers to charge or discharge of the battery in 1 h) is applied for duration of 60 s and the cell is then allowed to reach equilibrium, a state at which the OCV remains almost constant with the variation of 0.01 V. This procedure is repeated at intervals of 10%