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Effect of temperature and charge stand on performance of lithium-ion polymer pouch cell

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ABSTRACT

The effect of temperature in the range of −20 °C to 60 °C and charge stand periods of 1 day, 7 days and 15 days on the discharge capacity of lithium-ion (Li-ion) polymer cells is investigated quantitatively. Commercial 3.2 Ah Li-ion polymer pouch cells with $LiCoO_2$ cathode and graphite anode were used as test systems. The cells were charged at a constant current of 1 C until the voltage reached 4.2 V, then stored at different temperatures from −20 °C to 60 °C for charge stand periods of 1 day, 7 days and 15 days and discharged at 1 C rate current until the cell voltage reached 3.0 V. Although the discharge capacity of these cells at and around room temperature is reasonable, at temperatures below 0 °C and above 50 °C the performance is poor. At −15 °C, −20 °C, 40 °C, 50 °C and 60 °C temperatures, the discharge capacities decreased with charge stand periods. The discharge capacities are not affected by the charge stand periods from −10 °C to 30 °C. To identify the reasons for the poor performance at sub-ambient temperatures, electrochemical impedance studies were carried out on a fresh cell. The impedance data are analyzed using an equivalent circuit and Zman fitting software and the impedance parameters are evaluated. The resistances corresponding to high frequency and low frequency of Nyquist impedance plot exhibit a strong dependence on temperatures. The kinetic parameter namely, apparent exchange current density is calculated and discussed.

1. Introduction

Batteries used for specific purposes (such as defence, space etc.) are required to satisfy stringent demands and withstand harsh environmental conditions, both during deployment as well as storage. Lithium-ion (Li-ion) polymer batteries have higher energy densities (~400 $Wh\,l^{-1}$) compared to other batteries and are replacing nickel–metal hydride (NiMH) batteries for use in portable devices such as laptops and smart phones, and also for hand-held devices in the power tool industry [1]. The high energy/power densities of Li-ion polymer batteries have also made them attractive sources of power in electric vehicles (EV) and hybrid electric vehicle (HEV), as they can provide longer driving range and higher acceleration. However, Li-ion battery pack poses a challenge in effective thermal management [2]. Self-discharge is a phenomenon in batteries in which internal chemical reactions reduce the stored charge of the battery without any connection between the electrodes. Self-discharge decreases the shelf-life of batteries and causes them to initially have less than a full charge when actually put to use. Self discharge rate of a battery is reported as a percentage loss of capacity per month or year. In general, the high power secondary batteries used for practice purposes in defence are limited to 15 days of charge stand under specified temperature conditions. Thus, the battery is required to be used within 15 days after the completion of charging which confirms the capacity of the cell during discharge must still be very high and all other performance criteria should be within acceptable limits. Less than 2% self discharge rate per month is expected for Li-ion batteries at room temperature [3]. Further, when deployed in underwater vehicles, the batteries are exposed to different environmental conditions, yet require retaining the basic electrical characteristics for specified charge stand periods. It is essential to analyze the temperature and time dependent effect on performance of batteries before they can be used in defence applications. Several national labs and groups [4–8] have studied the storage of lithium-ion batteries. Wright et al. [4] observed a square root of time dependence of resistance of the cells, when they are stored for long period of time. When a cell is operated at high and low temperatures, there are various degradation processes that take place in different components as functions of operating conditions. One of the identified causes for degradation is the side reactions caused by reduction of electrolyte [9–11]. In general Li-ion

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batteries exhibit poor low temperature performance. Electrochemical aspects related to poor performance of Li-ion batteries at low temperatures have extensively been studied in recent years. Majority research is devoted to boost electrolyte performance towards lower freezing point and higher conductivity by using different solvent mixtures and novel electrolytes [12–17]. A combined experimental and modeling approach is applied and validated against Li-ion cells over a wide range of temperatures (−20 °C to 45 °C) and discharge rates [18]. Studies by Huang et al. suggest that the primary cause of poor Li-ion cell performance at low temperature is related to Li-ion diffusion in the carbon anode [19]. The behavior of lithiated graphite is studied combined with operando electrochemical and neutron powder diffraction at low temperature [20]. A formation of lithium plating at low temperatures is widely discussed in literature as another reason for limited cell performance [21,22]. Usage of Li-ion batteries at high temperature can lead to shortened lifetimes or catastrophic failures of batteries via thermal runaway that result in fire hazard and possible explosion in extreme cases [23]. Temperature dependent aging mechanisms in Li-ion batteries are estimated by Arrhenius plots in two different ranges of −20 °C to 25 °C and 25 °C to 70 °C [24]. Calendar life study of Li-ion pouch cells reveals that the anode experiences a severe loss of active carbon during storage, especially at high temperatures. The severe carbon loss could be caused by isolation of carbon particles by mechanical failure [25]. The time-dependent contribution of internal resistance to cell capacity during the course of cell operation is not fully understood.

Electrochemical impedance spectroscopy is utilized by many researchers to characterize each factor of batteries because it enables us to analyze the dynamics of each elemental step sensitively and separately without destruction of the cell [26–29]. In Nyquist plot of Li-ion battery impedance is reported to have semicircles in low frequency range and middle frequency range. The impedance spectra obtained at the temperatures between −20 °C and 20 °C show drastic change in sizes with shifting of the characteristic frequency and the SEI element is remarkably detected as a semicircle below 0 °C [30].

2. Experimental

Li-ion polymer (LIP) pouch cells of 3.2 Ah capacity (Kokam make model no. SLB8043128H) with $LiCoO_2$ cathodes and graphite anodes were used. In the present study, 33 nos. of above mentioned cells with similar mass, open circuit voltage, internal resistance and capacity at SOH = 100% were taken. Cells were divided into 11 groups, each group containing 3 nos. of cells. CC charging of cells was done using Powertronics (60 V/10A) DC power supply. The operating voltage of these Li-ion polymer pouch cells is 3.0 to 4.2 V. The cells were charged at a constant current of 3.2 A (1 C) until the voltage reached 4.2 V. Following this, a constant voltage charging maintained the voltage at 4.2 V until the current decayed to 100 mA. On completion of charge, the cells were kept in the Enviro-Tech (−30 °C to 100 °C) climatic chamber immediately. The cells were stored at different temperatures between −20 °C to 60 °C (*i.e.*, −20, −15, −10, −5, 0, 10, 20, 30, 40, 50 and 60 °C). They were stored for 1 day, 7 days and 15 days of charge stand periods inside the climatic chamber. On completion of respective time intervals, the cells stored at different temperatures were discharged at 3.2 A (1C rate) current until the cell voltage reached 3.0 V. Arrangements were made in such a way that the cells were discharged *in situ* in the temperature chamber itself. This was done to ensure that the same temperature was maintained even during their discharge. Programmable DC electronic load bank (Model ELHC-1200) was pre-connected for discharging the cells.

Electrochemical impedance measurement was carried out on a fresh 3.2 Ah SLB8043128H Li-ion polymer pouch cell using IVIUM Potentiostat/Galvanostat instrument. Charging of this cell was carried out as per procedure mentioned above. EIS measurement was started on a fully charged (100% SOC) cell at 20 °C with 6 h equilibration time in the climatic chamber. The frequency domain of investigation ranged from 100 kHz to 10 mHz in automatic sweep mode from high to low frequencies with a frequency distribution of 10 frequencies/decade and ac perturbation amplitude of 10 mV. The impedance spectra were subsequently obtained at each temperature (60 °C, 0 °C & −20 °C) with 6 h equilibration time. Data acquisition and analysis were done using the Zman software.

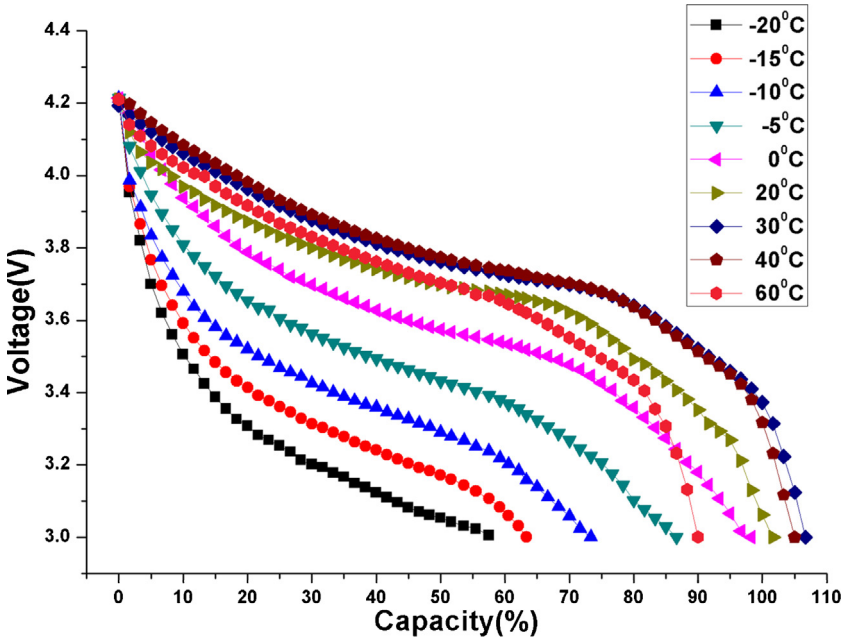

Fig. 1. Discharge plots of LIP cells stored at different temperatures for 1 day.