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Study of Electrical and Thermal Behaviour of *Li*-ion Polymer Cells for Auxiliary Power Supply in Underwater Applications

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ABSTRACT

Lithium ion polymer (*Li*-Po) battery technology is the latest technology for portable use and the most promising technology for exercise torpedoes. These batteries are technologically evolved from Lithium ion batteries. In this paper, extensive experimental studies on *Li*-Po cells which include studies on electrical characteristics during charge-discharge cycles, discharge at different C rates, self discharge throughout charge stand, temperature profiles at the cathode and anode during the discharges, etc. are reported and discussed. The extensive electrical characterisation done on these cells indicates the capability of these cells for use as auxiliary power supply in underwater weapon applications.

Keywords: *Li*-ion, volumetric and geometric energy densities, self discharge

1. INTRODUCTION

Lithium-ion (*Li*-ion) is the most promising battery technology for underwater applications, because of their high energy density and cost effectiveness. *Li*-ion holds the highest volumetric and gravimetric energy densities among the rechargeable chemistries[1,2]. These cells can be tailor made into a wide variety of shapes and sizes depending on the specific applications. These are lighter and low maintenance batteries (sealed cells). Since the nominal cell voltage of *Li*-ion cell (3.7 V) is high as compared to other batteries such as Nickel-Cadmium, lead acid, etc., less number of cells are required to be packed for obtaining a particular voltage. They are cost effective because of high cycle life. Only need is the protection circuitry to safely sustain against the physical or electrical abuse.

Technological advancement of *Li*-ion is the 'Lithium-ion polymer' (*Li*-poly or *Li*-Po). It is a *Li*-ion cell which consists of gelled polymer electrolyte[3].

This polymeric electrolyte is impregnated over the porous separator[4]. The major advantage of *Li*-Po battery is its wafer thin geometry. Unlike *Li*-ion cylindrical or prismatic cells, with a rigid metal case, polymer cells have a lower weight, large foot print, flexible, foil-type case and exclusively packaged in so-called 'pouch cell' in which the traditional metallic cylindrical can is replaced with an inexpensive foil packaging that can be specifically shaped to fit the device it powers. Because of the less dense packing and the lack of metal casing, the energy density of *Li*-Po batteries are higher than that of a classical *Li*-ion battery. *Li*-Po cells have improved safety features than *Li*-ion cells[3].

Li-Po cells employ lithium intercalation compounds as the positive and negative electrode materials. Positive electrode material is a metal oxide with a layered structure[5,6], such as $LiCoO_2$, $LiNiO_2$, $LiNi_{1-x}Co_xO_2$ on a current collector of aluminium foil. Negative electrode material is graphite carbon which also has a layered structure similar to graphite on a copper current collector. The electrochemically active electrode materials adhere to their respective metal foil current collectors with a binder typically poly vinylidene fluoride (PVDF) or poly vinylidene fluoride-hexa fluro propylene (PVDF-HFP). Lithium batteries are sealed cells and use non-aqueous solvents as electrolytes because of the reactivity of lithium in aqueous solutions. As the cells are sensitive to overcharge and over discharge, an electronic protection circuit is essential to avoid the deterioration of cells and explosion hazards.

2. EXPERIMENTAL

The electrical and thermal parameters of 40 A hr (Ah) capacity *Li*-Po cells were evaluated to assess the suitability as an auxiliary power source for underwater applications. Although, the cells are rated as 40 Ah cells, the initial input and output capacities realised during charge and discharge respectively a more than 40 Ah. More active material is packed into the cells to realise the rated capacity even towards the end of the shelf life of the cells. Thus, higher capacities are realised in the initial stages of use of the cells. To conduct the study on *Li*-Po cells, six cells named V_1, V_2, V_3, V_4, V_5, and V_6 procured from the trade were selected. Three of the cells viz., V_1, V_2, and V_3 were connected in series as shown in Fig.1 and named as 'Pack-1'.

Similarly, V_4, V_5, and V_6 were connected in series and named as 'Pack-2'. Two types of cycling, namely 'normal' cycling and 'quick' cycling were tried to study the nature of the cells. Normal cycling is the procedure in which each cell in Pack-1 is charged up to 4.2 V (cut off voltage) at 10 A current and discharged at 40 A (1 C rate) current after 15 days charge stand period. After discharge and stabilisation

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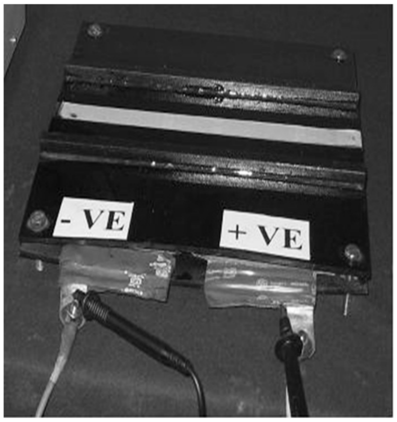

Figure 1. Li-ion polymer pack.

for one day (without discharge stand period), it was fully charged again and kept in charge stand. Quick cycling is chosen to complete more number of cycles in less time. It is the procedure in which each cell in Pack 2 is charged up to 4.2 V at 10 A and discharged on the next day after voltage gets stabilised. Experimental set-up to charge and discharge was same for both normal cycling and quick cycling.

2.1 Discharge of Cells at Different C Rates

To establish the performance of *Li*-Po cells, 40 Ah cells were discharged at different currents varying from 20 A (0.5 C) to 200 A (5 C). Three cells were charged initially to an input capacity of approximately 42 Ah and discharged at low rates of discharge of 20 A (0.5 C), 40 A (1 C) and 80 A (2 C) manually using rheostats approximately for 2.0 h, 1.0 h, and 0.5 h, respectively. The output capacities realised were 40.4 Ah, 40.3 Ah, and 40.0 Ah respectively for 0.5 C, 1 C, and 2 C rates of discharge.

Three more cells were taken up for study of discharge at higher rates beyond 2 C and presented as high rate discharge profiles. Initially, these three cells were charged to input capacities of 41.5 Ah, 42.0 Ah, and 42.1 Ah and were discharged at 120 A (3 C), 160 A (4 C) and 200 A (5 C) for discharge periods of about 20 min, 15 min, and 12 min respectively. The realised output capacities were 40.8 Ah, 41.0 Ah and 40.6 Ah respectively for 3 C, 4 C, and 5 C rates. The cells were discharged with the help of programmable electronic load bank having provision for constant current discharge. The experimental setup for charge and discharge can be seen from Figs 2 and 3 respectively.

Figure 2. Experimental set-up for charging.

Figure 3. Experimental set-up for discharge.

2.2 Temperature Profiles During Discharge

Rise in temperature during discharge of *Li*-Po cells are one important criterion considered while adapting it for weapon applications. To measure and monitor the temperature of 40 Ah cells during discharge, few experiments were conducted with three new cells. Temperature sensors (Chromel-Alumel Thermocouple) were positioned at their cathode and anode terminals as the terminals of the cell are the extensions of the grids of cathode and anode which collect the current generated. Inside the cell, the chemical reactions take place at the electrodes. Hence, the temperature changes in the cell can be sensed by placing temperature sensors at the terminals. These cells were charged fully and then discharged at different rates from 1 C to 5 C to monitor the rise in temperatures at anode and cathode terminals independently.

The temperatures of the cathode and anode during the discharges from 1 C to 4 C rate were monitored. After the 4 C rate discharge, the cells were charged and then discharged at 1 C rate to check their health. After establishing 4 C capability, the cells were subjected to 5 C discharge, i.e., at 200 A. This was again followed by charge and discharge of the cell at 1 C rate to find out their condition.

3. RESULTS AND DISCUSSION

The 40 Ah *Li*-Po cells were subjected to exhaustive testing to evaluate their electrical and thermal performance. The typical charge-discharge characteristics of pack 1 under normal cycling can be seen from Fig. 4. As can be seen from the charging plot, the voltage of the cells raises from about 3.4 V to 4.2 V which is the cut off voltage of the *Li*-Po cell more or less linearly in about 4 h, when charged at 10 A current.

When the cells were discharged at the rate of 40 A after the charge stand period of 15 days, the cell voltages fell from about 4.2 V to 3.2 V in about 1.2 h. As can be seen the fall in voltage is also linear. Similarly, the voltage rise and fall under quick cycling procedure can be seen during charge and discharge in Fig.5. As can be seen from the plots of normal cycling and quick cycling, the patterns of voltage build up during charge and fall in voltage during discharge follow similar pattern. Hence, scheduled cycling is not required to improve the performance of the cell.

3.1 Discharge of Cell at Different C Rates

Discharge profiles are shown in Fig. 6. The figure shows the combined profiles of low rate discharges 0.5 C, 1 C, 2 C

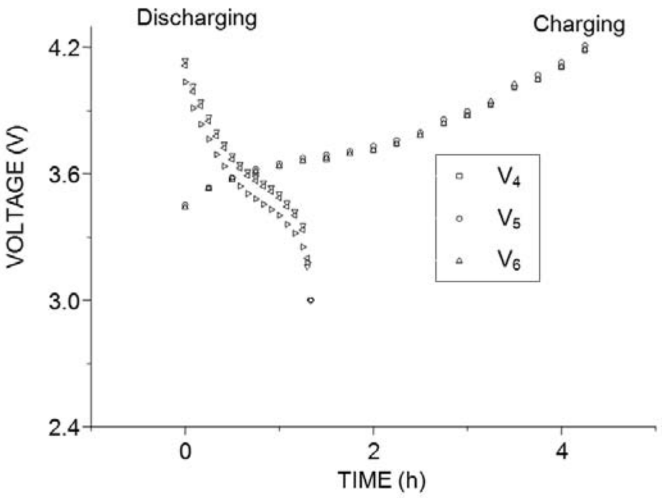

Figure 4. Typical charge-discharge characteristics under normal cycling.

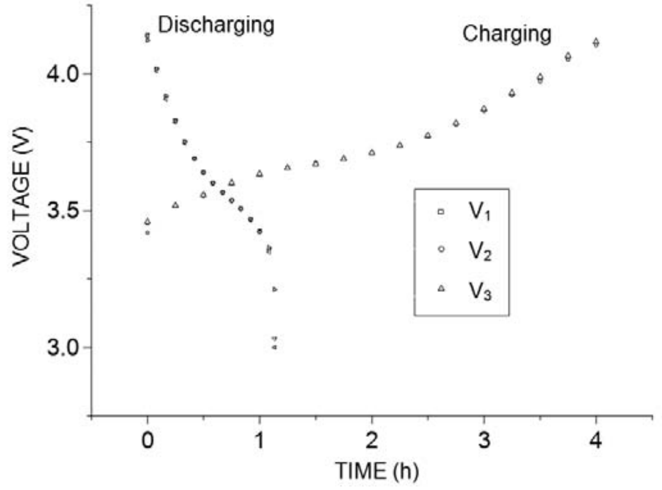

Figure 5. Typical charge-discharge characteristics under quick cycling.

and high rate discharges 3 C, 4 C, 5 C.

As can be seen from the plot, the discharge durations were nearly 2 h, 1 h, and 0.5 h for 0.5 C, 1 C, and 2 C rate discharges. The realised capacity of cell discharged at 0.5 C rate (41.50 Ah) is marginally better than the other two. Similarly, the cell discharged at 1 C rate (41.00 Ah) realised better performance over the cell discharged at 2 C rate (40.25 Ah). This can be attributed to the reason that the cells when discharged at low currents lose very less energy in terms of heat[1]. Other parameters like different external boundary conditions and kinetic parameters also influence this behaviour[7]. Thus, higher capacities can be realised from the same cell when discharged at low rate. As can be seen from the plot, the realised capacity reduced gradually when discharged at 3 C rate (40.00 Ah), 4 C rate (38.25 Ah) and 5 C (36.00 Ah) rate for the same reasons discussed above. However, the profiles of voltage fall with time still remain the same and are very stable.

3.4 Temperature Profiles During Discharge

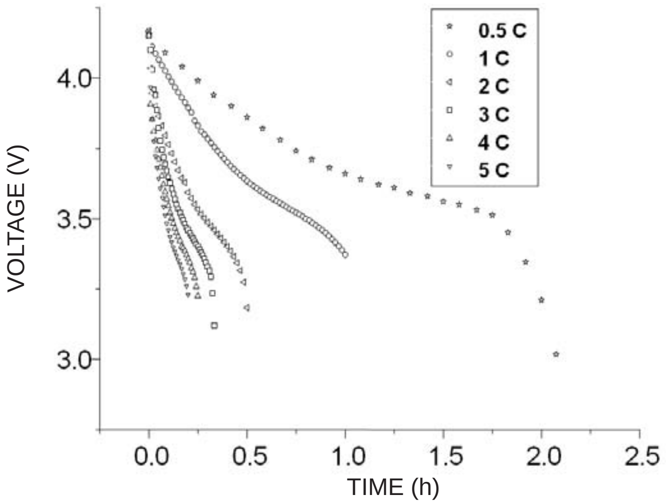

Figure 6. Fall in voltage with time for different rates of discharge.

The typical temperature profiles of cells discharged at 1 C, 2 C, 3 C, 4 C, and 5 C rates are shown in Fig.7, which shows the temperatures recorded at the cathode and anode. As can be seen from the Fig. 7, during 1 C discharge, temperature is observed to be stabilised at approximately 36 °C and 39 °C respectively at anode and cathode within about 35 minutes, even though the discharge was carried out for the stipulated time period of one hour. Thus, the temperature profile is shown up to 35 minutes only in the figure. When the cells were discharged at 2 C, 3 C, 4 C, and 5 C rates the maximum temperatures recorded at cathode were 45 °C, 50 °C, 61 °C, and 68 °C by the time the cell voltages reached the minimum permissible voltage of 3.0 V. The cells were discharged up to 30 min, 20 min, 15 min, and 12 min respectively to exhaust the input capacity fully.

Similarly, the temperatures recorded at anode were 42 °C, 46 °C, 55 °C, and 61 °C. As can be observed, the temperatures recorded at the cathode terminal are higher than those recorded at anode at all rates of discharge. It is pertinent to mention that the temperatures of cathode and anode nearly reached the safety limits (65 °C) when discharged at 5 C rates, where the breakdown of the organic solvents used in the electrolyte takes place, typically at 70 °C[1,2]. During the temperature measurements, it is observed that the ambient temperature has played an important role in the increase of electrode temperatures and performance of cell. As room temperatures are above 30 °C in the Indian scenario, it is safe to operate the cells up to 4 C rate, so that irreversible damages will not occur inside the cells and failures can be avoided.

The reasons for different temperatures recorded at anode and cathode can be explained as follows. The cathode terminal is made of aluminium while the anode terminal is of copper material. In all the above temperature profiles, it is found that the temperature at cathode was always more than that of temperature at anode terminal. This behaviour could be due to the reasons that the electrical resistivity and thermal conductivity of aluminium are 28.20 nΩ-m (20 °C) and 237.00 $Wm^{-1}k^{-1}$ (27 °C) respectively while that of copper are 16.78 nΩ-m (20 °C) and 401.00 $Wm^{-1}k^{-1}$ (27 °C). Higher resistance and lower conductivity of aluminium terminal result in faster rise in temperature. Hence, aluminium cathode shows slightly higher temperatures as compared to copper anode[8]. The second reason

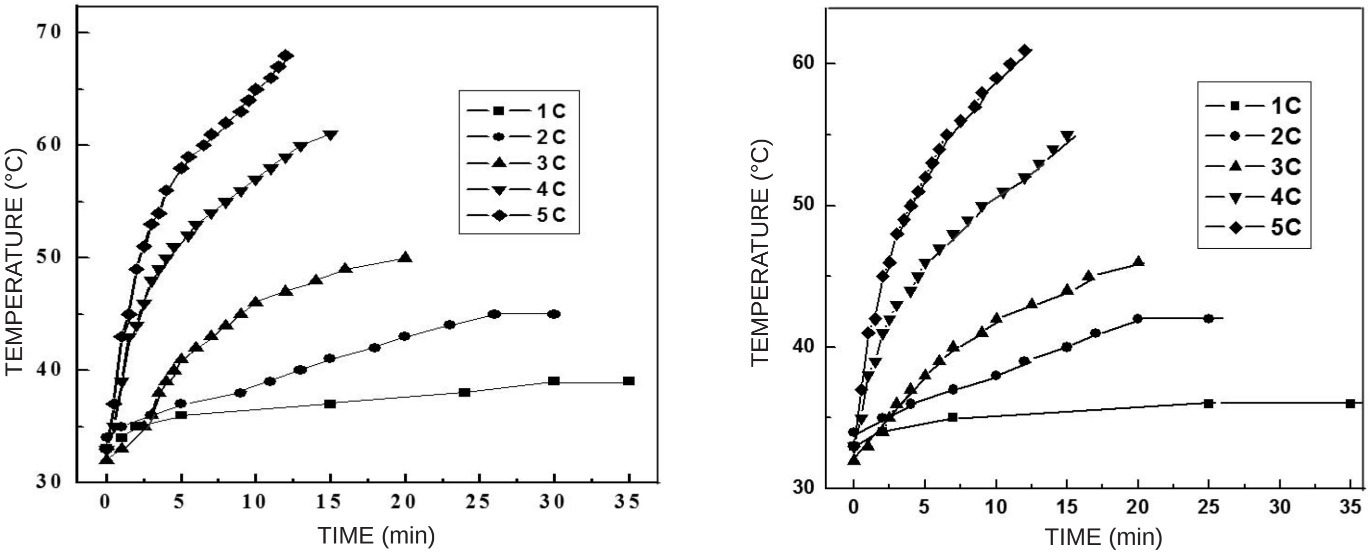

Figure 7. Rise in temperatures of anode and cathode of cells during discharges at 1C, 2C, 3C, 4C, and 5C rates: (a) temperature rise at cathode, (b) temperature rise at anode.

could be that $LiCoO_2$ is a p-type semiconductor with band gap $E_g = 2.7eV$ while $Li_{1-x}CoO_2$ for $x \leq 0.75$ has a metal like behaviour whereas there is no change in the phase of graphitic carbon during charging and discharging which is a semiconductor. $Li_{1-x}CoO_2$ is predicted to have partially filled valence bands for $x < 1$. For every Li removed from $LiCoO_2$ lattice, an electron hole is created within the valence band. For $x \leq 0.75$, it is expected that there are sufficient holes to allow for a significant degree of screening and in this regime, the hole states in valence band are likely to be delocalised such that $Li_{1-x}CoO_2$ exhibits metallic electronic properties. This behaviour is clearly observed in FTIR absorption spectra where absorption by holes is observed[9]. Thus, $LiCoO_2$ is a p-type semiconductor initially. In charging Li^+ ions are removed from $LiCoO_2$. During this process it gets converted into $Li_{1-x}CoO_2$ and starts exhibiting metal like properties. Hence, the electrical resistance of the cathode decreases by the end of charging. During discharge Li^+ ions are inserted back into $Li_{1-x}CoO_2$, which becomes again $LiCoO_2$. Therefore, the electrical resistance of cathode increases during the discharge as the cathode material is now being converted into semiconductor from metal. As the electrical resistance increases, the heat production at the cathode also increases which leads to higher temperature at cathode.

4. CONCLUSIONS

Extensive electrical characterisation of *Li*-Po cells indicate that:

1. These cells do not have specific charge stand periods and they are capable of providing high discharge currents up to 5 C rate.
2. *Li*-Po cells can be used for weapon applications for auxiliary power supply and can be configured to be discharged up to 4 C rate in the Indian scenario, where room temperatures are above 30 °C or till cell temperature reaches the safety limit of 65 °C.
3. The temperature profiles of cathode terminal and anode terminal are recorded for safe operation of cells when discharged at different rates from 1 C to 5 C. Rise in temperature at a cathode terminal is greater than that at anode terminal.

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