

Galvanostatic Discharge of Lithium MnO₂ Button Cell: A Case Study

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Abstract

CR2032 button cells were fabricated in the laboratory with chemically prepared MnO₂ cathode and lithium anode containing LiAlCl₄ in PC (propylene carbonate) as electrolyte. These cells were discharged at various currents (15 mA, 20 mA, 25 mA, 30 mA, 35 mA and 40 mA) for various temperatures (0, 10, 30, 40, 50 and 60 °C) galvanostatically. The results are discussed in detail.

Keywords: lithium cell, galvanostatic method, cell discharge, non-aqueous electrolyte.

Introduction

Lithium MnO₂ [1,8] systems are well known for more than one and a half decades and have been widely studied and used in many electronic gadgets useful to society. MnO₂ is available in plenty in nature and also a cheap material. MnO₂ exists in alpha, beta, gamma and delta phases. Although gamma MnO₂ is well established as a cathode in aqueous [4] and in non-aqueous media [1,2,3], the efficacy of other forms of MnO₂ was tried. Several publications pertaining to use MnO₂ [5,6] in non-aqueous media are available in the literature for lithium MnO₂ button cell. A novel [5] method has been tried to prepare MnO₂ chemically and this MnO₂ has been used in our button cell CR2032. While fabricating cell in the laboratory, PC or mixture of PC/EC [7] and gamma butyrolactone and several non-aqueous solvents [8] were tried and the discharge studies were carried out for Li/MnO₂ system. Light and heavy discharges were made under galvanostatic conditions for MnO₂ systems with LiClO₄ [9] as electrolyte. Li/MnO₂ cells are commercially used and produced in large quantities for small cell applications.

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Chemicals and materials

Propylene carbonate

Propylene carbonate is distilled twice under vacuum and the distillate is stored in a suitable vessel. This solvent is treated with molecular sieves (4 Å) so as to bring down the water content to 50 ppm. The water content of the solvent is now and then estimated by IR spectrophotometer, calibrated for analysis or using Karl Fischer method of titration.

Lithium tetrachloro aluminate (LiAlCl₄)

In the literature, the method of preparation of LiAlCl₄ is available by mixing equimolecular proportions of lithium chloride (dried) and aluminium chloride (dried) by heating it at 300 °C to get LiAlCl₄ [7]. Another method of preparation available in the literature is to mix dried LiCl and AlCl₃ in equimolecular proportions and dissolve the mixture in PC.

Instead of these methods, a novel method developed by Gandharan [10] is tried in this experiment. Lithium aluminum hydride (LiAlH₄) is taken carefully in a dry box and a portion of this compound is transferred in a China dish kept in a closed tube and dried chlorine gas was passed slowly over the LiAlH₄ kept in the tube to convert to LiAlCl₄ directly. This compound is dissolved in PC. The whole process of dissolution was carried out in a glove box.

MnO₂

Manganese dioxide is available in different forms. However, in the laboratory we have prepared MnO₂ by heating KMnO₄ at 1000 °C temperature under vacuum for 8 hours and the product was washed in dilute [10⁻² N] HNO₃ to remove potassium salts and the MnO₂ left out which is a mixture of beta and gamma form which is used for our experiment.

Separator

Polypropylene separators available in the market for battery purposes (cell guard) are used for experimental purpose.

Button cell

We have fabricated from our workshop button cell components made of 316 stainless steel plates for type CR2032 cells and polypropylene o-washers were made. Leak proof button cells were fabricated using these containers and rings.

Preparation of the solution

A calculated quantity of dried LiAlCl₄ is dissolved in distilled PC so as to make one molar solution.

Preparation of the cathode

MnO₂ prepared from KMnO₄ is mixed with acetylene black in the ratio 9:1 and this mixture is kept in acetone. To this, 1% solution of colloidal Teflon was

added and the whole mixture was slowly evaporated to dryness and then the mixture was dried in an air oven kept at a temperature of 100 °C for 2 hours and the dried product was spread over a circular Ni mesh cut to dimensions of CR2032 button cells and applied a pressure of 10 Kg/m² on a hydraulic press to get MnO₂ cathode.

Fabrication of button cell

A button cell was fabricated in a glove box with lithium metal spread over a Ni mesh above which a separator was kept and over which the cathode was laid. The whole cathode-anode assembly was kept in a button cell. The whole button cell after adding the electrolyte was carefully sealed. Thus an assembly of a cell was made.

Galvanostatic discharges

Several button cells of CR2032 assembled under the same conditions described above and galvanostatic discharge studies were carried out at various currents (15 mA, 20 mA, 25 mA, 30 mA, 35 mA and 40 mA) in different temperatures (0 °C, 10 °C, 30 °C, 40 °C, 50 °C and 60 °C). Digital multimeters and thermometers were used for the purpose of measuring current and temperature during galvanostatic discharge studies.

Discussion

A series of experiments were conducted with fabricated Li cells. In order to study the behavior of the cell at various currents, the cell voltages and time were recorded. In other words, E-I curves were drawn for various cells at various temperatures under galvanostatic conditions.

The results are drawn in the form of graphs. It is possible to conclude the economical viability of withdrawing the current within the decided voltage of a cell. The E-t curves help us to know how much amount of current can be withdrawn within the cut-off voltage of the cell.

Interpretation of the E-t curves from the experimental results

The voltage curves for the discharge study of CR2032 cells at galvanostatic conditions, namely 15 mA, 20 mA, 25 mA, 30 mA, 35 mA and 40 mA currents, and at various temperatures of 0 °C, 10 °C, 30 °C, 40 °C, 50 °C and 60 °C, are shown in Fig 1.1 to Fig 1.6.

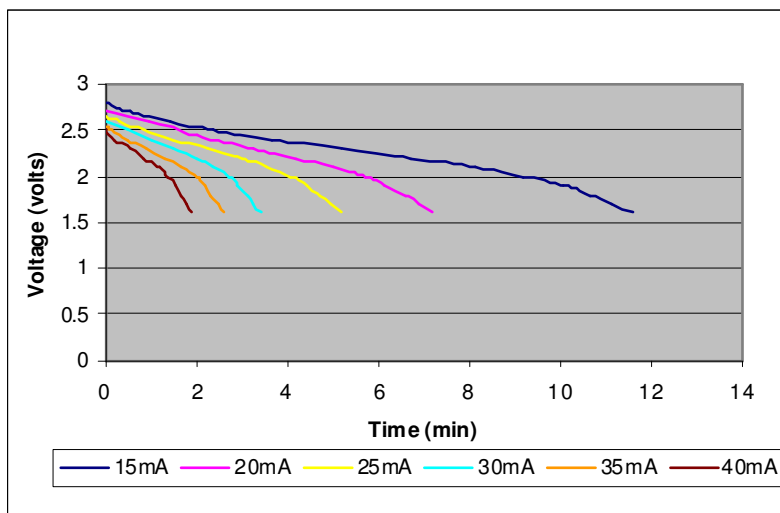


Figure 1.1. E-t curves at 0 °C for different currents.

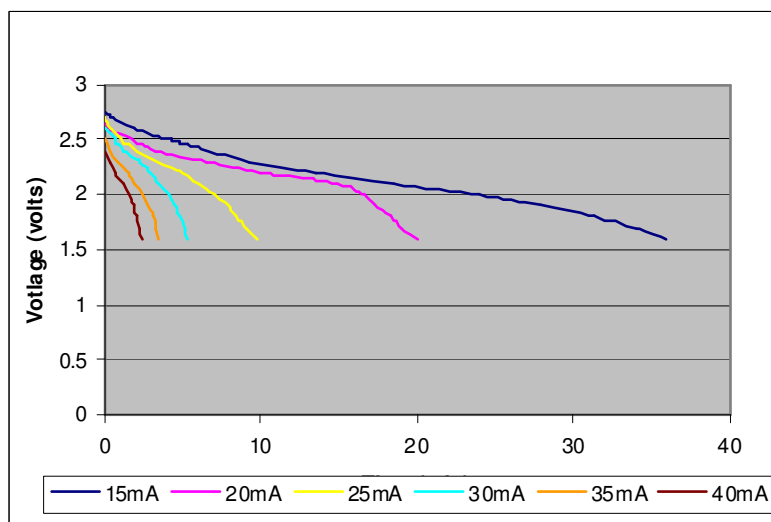


Figure 1.2. E-t curves at 10 °C for different currents.

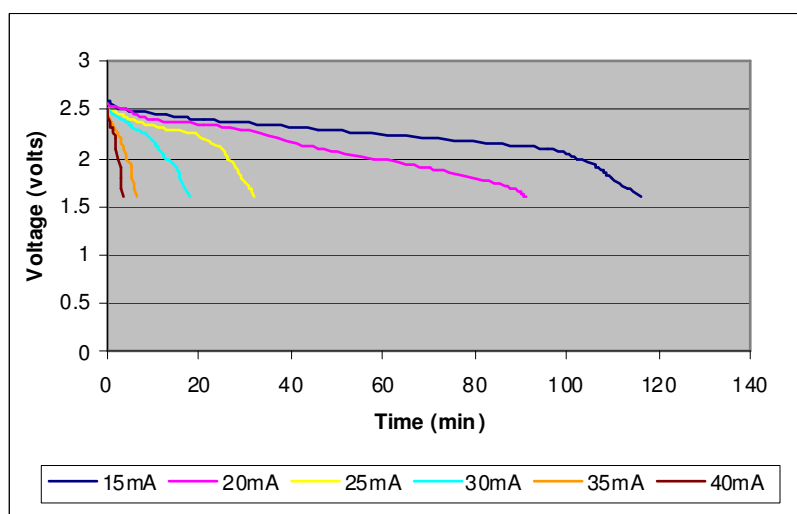


Figure 1.3. E-t curves at 32 °C for different currents.

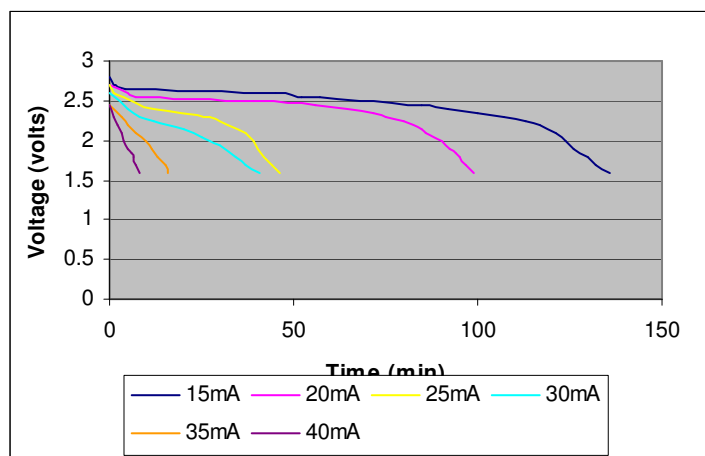


Figure 1.4. E-t curves at 40 °C for different currents.

At high discharge rates, the cell is not able to deliver current for a long time and the efficiency of the cell reduces considerably due to various over-potentials associated with it, namely; diffusion, resistance and ohmic over-potentials.

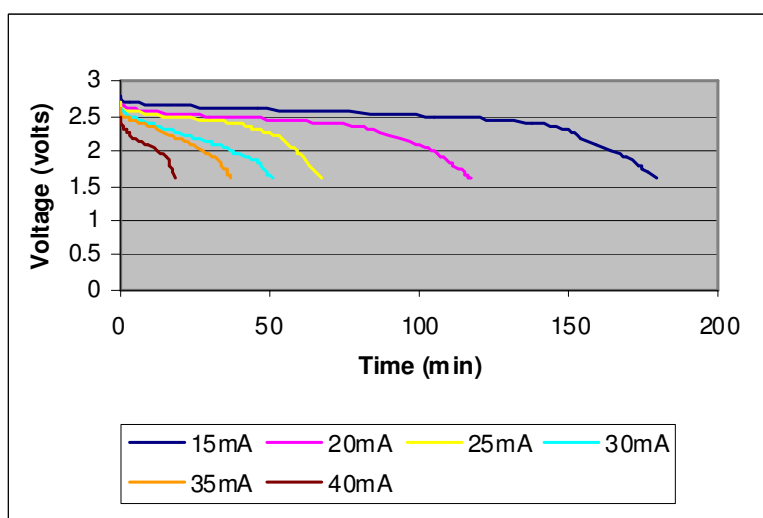


Figure 1.5. E-t curves at 50 °C for different currents.

An interesting result has been observed during the course of the experiments. When constant current discharges were made for the cells at various temperatures, on contrary to the expectations, it was observed from figures 1.1 to 1.6, that at low temperatures the discharge was poor but at high temperatures it took longer time to discharge. This phenomenon is uniformly observed for various currents. These results are unique and are contrary to the expectation of an aqueous cell system. The reason for such reversal of behaviour can be attributed to the following:

1. The solubility of the electrolyte decreases with decrease in temperature and because of this the concentration of the electrolyte in the medium falls, and this fall is responsible for decrease in conductivity and due to this the time of discharge reduces at low temperature.

- As a result of the above phenomenon, the internal resistance of the cell increases at low temperatures and at high temperatures it decreases. This is uniformly observed for various currents. Also, at the same temperature, the discharge time decreases for higher currents.

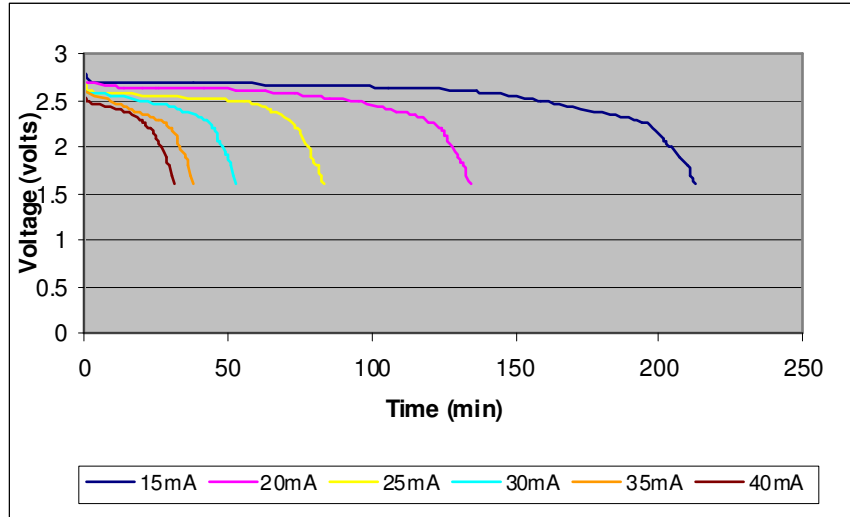


Figure 1.6. E-t curves at 60 °C for different currents.

Interpretation of E-I curve from the experimental results

E-I curves for various temperatures were drawn and it is observed that a linear curve is obtained uniformly for different temperatures. Generally E-I curve is hyperbolic in nature in aqueous solutions but the observation from our experiments are contrary to the expectations of an aqueous system. The reason for the linearity of the curve is due to a decade less in conductivity in non-aqueous solutions as compared to aqueous media.

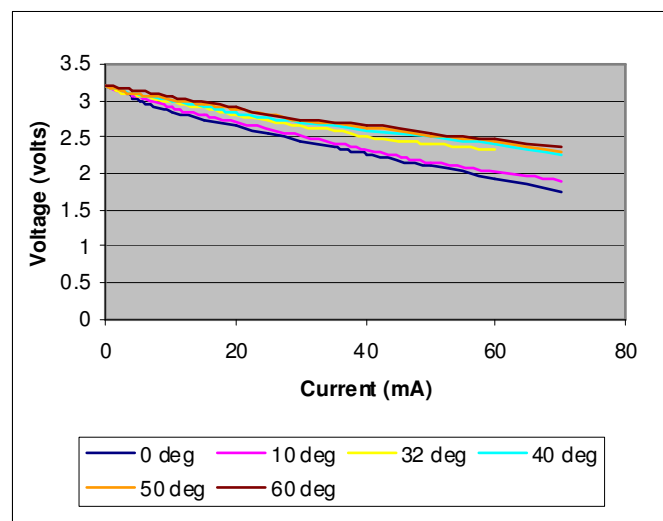


Figure 2. E-I curves at different temperatures.

The experimental results are recorded and the E-I curves are drawn as shown in Fig 2. From the figure it can be observed that there is a greater fall of discharge curve at lower temperature than at higher temperature, which also indicates that the conductivity decreases with decrease in temperature. This also explains that the internal resistance decreases with increase in temperature and this permit to draw more current at high temperature than at lower temperature.

Temperature vs. time and current vs. time for cut-off voltage of 2 V

We have fixed the cut-off voltage for discharge studies as 2 V for economic withdrawal of current from the cell. From the results obtained, the temperature vs. time (Fig 3.1) and current vs. time (Fig 3.2) graphs were drawn for cut-off voltage of 2 V. Here also, the time of discharge is more at high temperature which indicates conductivity increases with temperature. However, at higher discharge rates the polarisability increases and hence the time of discharge decreases which results in increase in inefficiency. This is expected because of side reactions and other additional over potentials associated with electrochemical process.

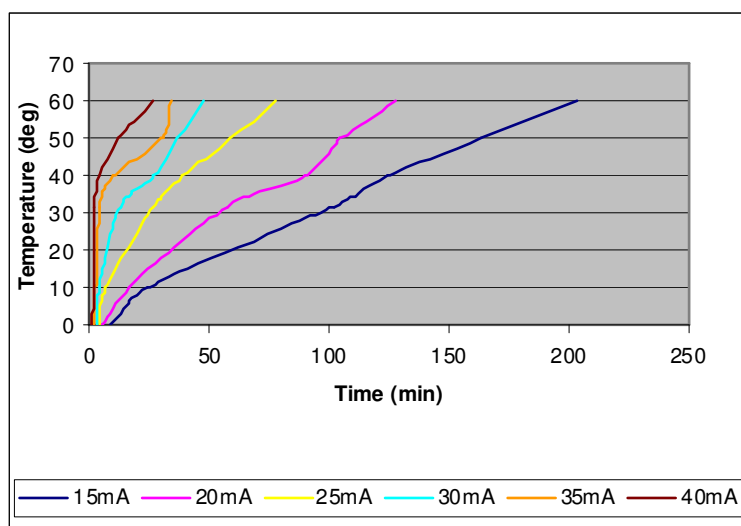


Figure 3.1. Temperature vs. time curves for cut off voltage of 2 V and for different currents.

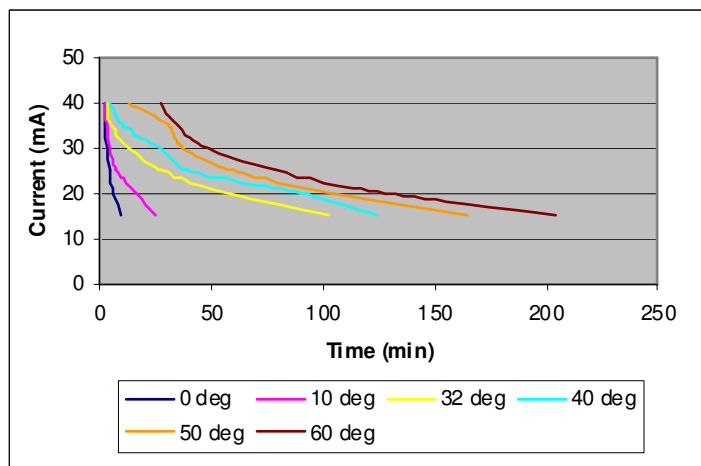


Figure 3.2. Current vs. time curves for cut off voltage of 2 V at different temperatures.

Conclusion

The discharge studies are carried out on a 3 V lithium button cell and following inferences are made from the studies:

- 1) E-I curves clearly indicate that at low temperatures, the internal resistance is high and goes on decreasing with increase in temperature.
- 2) For the given cell, the E-t curves at a constant temperature indicate that the internal resistance decreases as the current decreases. This phenomenon is due to the presence of non-aqueous media in a lithium cell.
- 3) E-t curves for constant currents show that the internal resistance decreases as the temperature increases.
- 4) The cut off voltage at different currents for the temperature-time curve shows that at high discharge rates, the inefficiency of the system increases with increase in discharge rate and it is greater at lower temperatures.

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