CHAPTER 6

BATTERY STUDY-ELECTROCHEMICAL APPLICATION

This chapter covers the battery application of the prepared optimized GPE membranes by using suitable anode and cathode materials. Measurement of discharge characteristics of fabricated battery is undertaken and extracted battery parameters are represented.

6.1 Introduction

A battery is a chemical device for the storage of electricity. Recent studies have now largely focused on the construction of solid-state devices with outstanding capabilities for energy storage [1]. Due to their possible demand in portable electronic devices, electric cars, hybrid electric vehicles (HEV), etc., lithium-ion batteries (LIBs) have received intensive attention across the global scientific communities. In the current scenario, gasoline vehicles are being replaced with electrical ones due to the greenhouse effect and global warming [2]. The main safety-related issues that occur in LIBs are ended up causing by cell expansion, short circuits, electrolyte leakage, flammability, the toxicity of materials, and electrolyte dissolution [3].

Li-ion battery has a vital combination of high power and energy density, making it the most choice in portable electronic devices. Li-ion batteries are costly at present and will

be having a shortage of Li and transition metals used for the battery fabrication becoming an issue to use in the long run. But Li-battery have also certain advantages such as low reduction potential, high cell potential, long life, lightest and small ionic radii, etc. Due to these factors, it imparts high volumetric capacity and power density [4]. The first-ever Li-ion battery was fabricated by using $LiCoO_2$ as a cathode, carbon as an anode, and non-aqueous electrolyte [4]. Then, so many researches have been done on the battery by taking different cathode material such as an oxide of lithium manganese, lithium nickel cobalt manganese oxide, lithium-ion phosphate, FeS_2, V_2O_5 and electronic conducting polymers [5]. The anode is the other part of the battery wherein the function of the battery also dependent on the properties of the anode material. The most common anode material is graphite but now a day's number of researches has been focusing on different material such as Sn, Si, SnO_2, Fe, Cu, Mn [6]. There are different types of the battery system. Two broad categories of the battery are (i) 'Primary batteries', the chemical present in it can be utilized once only in a single discharge and (ii) 'Secondary batteries' which can be recharged and utilized again.

6.2 Working Principle of The Battery

The battery mainly consists of electrodes i.e., anode, cathode and electrolytes. Anode, at which oxidation process occurs i.e., loss of electrons, and a cathode where reduction process takes place i.e., a gain of electrons. Electrodes are the source of electrons involved in an electrochemical reaction that provides electronic current to the outer circuit. Electrolytes are electronic insulators, but allow to flow of ions through them and prevent contact of anode and cathode. The construction diagram of the battery is shown in Figure 6.1. The basic principle of lithium-ion battery is based on the intercalation and de-intercalation of lithium-ion into electrodes. Due to the potential difference between the two electrodes, the battery function as an electrochemical cell.

At the time of the charging and discharging process, electron flow through the external circuit from an anode to the cathode side, simultaneously Li^+ ion travel through the electrolyte between two electrodes in the same direction as the electrons travel through an external circuit. Thus, whatever electrochemical energy stored within the system is converted in the form of electrical energy.

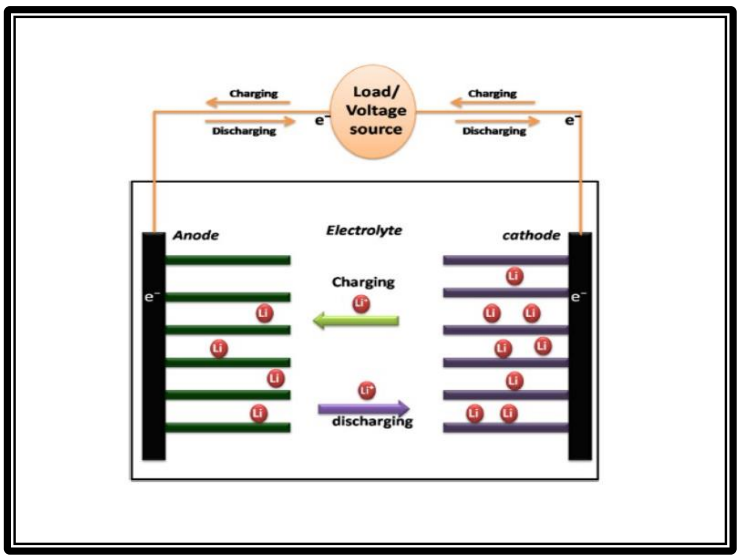


Figure 6.1 The construction diagram of battery [7]

The performance of the battery mainly depends on the properties of electrolytes and electrodes which are used for the fabrication of the battery. The ideal polymer electrolyte should meet the following requirements:

- High ionic conductivity close to liquid electrolytes (10^{-4}-10^{-3} S cm^{-1} at RT);
- High ionic transference number;
- Low interfacial resistance;
- Excellent thermal and electrochemical stability;
- Appreciable mechanical strength.

The second component, electrodes, on which a number of researches have been done to improve the function of an electrochemical battery such as specific energy, specific power, discharge capacity, etc. Carbon has been the most promising candidate as an electrode in energy storage devices due to its excellent electronic conductivity, inexpensive, higher mechanical stability, large surface area. Nevertheless, high energy loss occurs during the charge-discharge cycle result in the reduction of the energy density. Metal-based electrodes are recommended to achieve higher energy density to overcome this problem because of their advantageous properties; e.g., high surface area, ease in terms of processibility. As compared to a system with Zn metal-based electrode, the high value of resistance has been reported by Perumal et. al [8] for the system with carbon as electrode because of the development of passivation layers at the electrode. As a cathode ,Vanadium pentoxide (V_2O_5) is known to be one of the conventional intercalation cathodes owing to its potential insertion properties [9]. The electrodes may also contain additives such as PVDF,

conducting polymer electrolytes which act as binder aid for ease preparation of electrodes, improve adhesive properties as well as improve mechanical strength.

In the present study battery discharge characteristics have been determined by fabricating a battery with an optimized electrolyte sample as a separator from each series and suitable anode and cathode materials as electrodes. During the discharge process of the battery, the terminal voltage or open-circuit voltage falls at a constant load. The typical discharge profile of the battery is depicted in Figure 6.2, The figure shows a discharge of battery at a high, medium, and low rate. The high discharge rate in which voltage drops quickly indicates only a part of the capacity can be used for small-time. The low discharge rate indicates large capacity can be utilized over a longer time. From the discharge profile, different parameters such as OCV, specific energy, specific power, discharge capacity, energy density, and power density are extracted to observe the function of the fabricated battery.

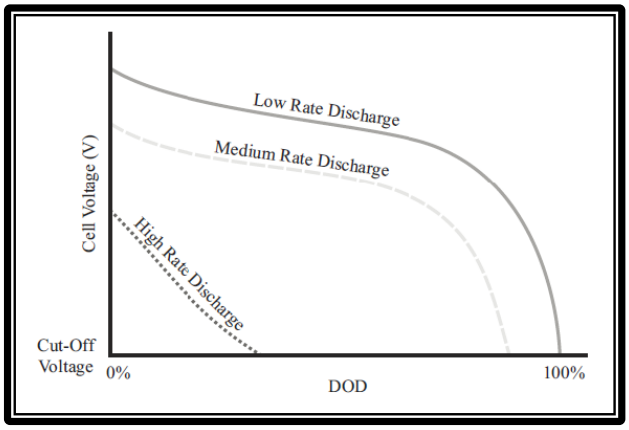


Figure 6.2 Typical discharge profile of battery [10]

Definition:

- **Open circuit voltage (OCV)**: The terminal voltage across the battery terminal when there is no load.
- **Specific energy (Wh/kg)**: The nominal battery energy per unit mass is also referred to as ‘gravimetric energy density’.
- **Specific power (W/kg)**: The maximum available power per unit mass.
- **Energy density (Wh/L)**: The nominal battery energy per unit volume, also referred to as ‘volumetric energy density’.
- **Power density(W/L)**: The maximum available power per unit volume.
- **Battery capacity**: It is the amount of electric charge which can be stored in a specific condition.

- **Specific capacity**: The capacity output of a battery per unit weight, usually expressed in Ah/kg.

6.3 Preparation of Electrode Materials and Fabrication of Li^+ Ion Conducting Primary Cell

In order to fabricate Li^+ ion conducting primary battery, the optimized sample from each series has been used as a separator because an ideal gel polymer electrolyte should meet the requirement for Li^+ based batteries in terms of high ionic conductivity, high ionic transport number, excellent electrochemical stability, low interfacial resistance, and enough mechanical strength. A separator is sandwiched between suitable electrodes, anode as a negative electrode, and cathode as a positive electrode. The fabricated batteries have been studied through discharge characteristics at different load resistances. The various parameters such as discharge capacity, specific power, and specific energy, etc. have been extracted to evaluate the performance of batteries.

6.3.1 Preparation of Electrodes Materials

Anode: In the present work, the anode material was prepared by taking Zinc dust (Zn), Zinc sulphate ($ZnSO_4.7H_2O$), and carbon(ratio 3:1:1)[11]. The said materials are taken in the required proportion and grinded thoroughly by using mortar pastel to mix material at the molecular level and to achieve a fine powder. Then the materials were pressed to form a pallet of a thickness ~1mm. Zinc (Zn) is also found as potential candidates owing to a specific capacity of 412 mAh/g [12].

Cathode: To prepare the cathode material, lead oxide (PbO_2), vanadium pentoxide (V_2O_5), graphite, and high conducting polymer electrolytes were taken in the required proportion (ration 8:2:1:0.5)[13]. V_2O_5 Vanadium pentoxide is a plausible candidate to have a high capacity, stable structure, and low cost of material [14]. Here, Graphite is used as a conducting agent to prevail electronic conductivity of electrodes, and polymer electrolytes serve as a binder and also reduces the electrode polarisation [15].

Anode reaction:

$$nZn + ZnSO_4 \cdot 7H_2O = Z_{n+1(}SO_4) \cdot (7-2n)H_2O \cdot 2n(OH) + 2nH^+ + 2\,ne^-$$

Cathode reaction:

$PbO_2 + 4H^+ + 2e^- = Pb^{2+} + 2H_2O$

$V_2O_5 + 6H^+ + 2e^- = 2VO^{2+} + 3H_2O$

The produced H^+ ions at the anode site during the reaction process repel the present Li^+ ion in the gel polymer electrolyte. As a result of this, Li^+ ions reach the cathode side through GPE via the hopping process.

6.3.2 Gel Polymer Electrolyte Used As a Separator

Following three gel polymer electrolytes film has been chosen from each series with optimized parameters shown in Table 6.1 which fulfill the requirement of batteries.

Table 6.1 Optimized parameters of gel polymer electrolyte from each series.

Sr. No.	Parameters	Series (a): PVDF-HFP: PMMA-PC: DEC-7.5 wt.% $LiClO_4$	Series (b): PVDF-HFP: PMMA - $LiClO_4$-60 wt.%PC: DEC	Series (c): PVDF-HFP: PMMA - $LiClO_4$-PC: DEC-2 wt.% Al_2O_3
1	Ionic conductivity	2.83×10^{-4} S cm^{-1}	3.97×10^{-4} S cm^{-1}	1.62×10^{-4} S cm^{-1}
2	Ionic transport number	0.99	0.99	0.99
3	Mechanical Strength	2.76 MPa	9.21 Mpa	11.78 Mpa
4	Electrochemical Stability window	4.40 V	4.89 V	6.00 V

6.3.3 Cell Configuration

The coin-shaped batteries were configured by pressing the gel polymer electrolyte membranes between anode and cathode. The cross-sectional view of the fabricated battery is depicted in Figure 6.3.

The configuration of the Lithium-ion primary batteries is:

Cell 1: Zn+ $ZnSO_4$:$7H_2O$+C | PVDF-HFP: PMMA-PC: DEC-7.5 wt.% $LiClO_4$|PbO_2+V_2O_5+C+PE

Cell 2: Zn+ $ZnSO_4$:$7H_2O$+C|PVDF-HFP: PMMA - $LiClO_4$-60 wt.%PC: DEC |PbO_2+V_2O_5+C+ PE

Cell 3: Zn+ $ZnSO_4$:$7H_2O$+C|PVDF-HFP: PMMA - $LiClO_4$-PC: DEC-2 wt.% Al_2O_3 |PbO_2+V_2O_5+C+PE

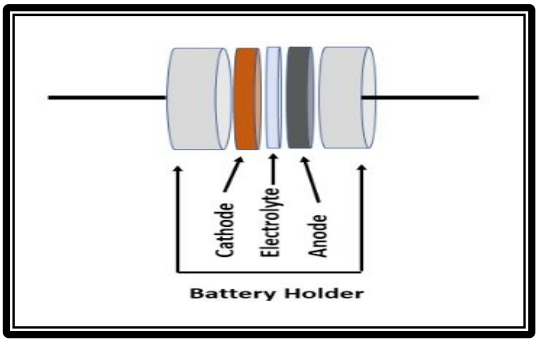


Figure 6.3 Schematic diagram or cross-sectional view of the fabricated battery.

6.4 Cell Characterization and Performance

The performance of cells has been evaluated by carrying out the following characteristics.

- Open circuit voltage (OCV)
- Discharge characteristics at different load resistance i.e. R = 4.8 KΩ, R = 10 KΩ and R = 21 KΩ

6.4.1 Open Circuit Voltage (OCV)

To estimate the initial voltage of the fabricated, open-circuit voltage (OCV) over a long period. The OCV values of 1.81 V, 1.84 V, and 1.8 V were obtained for cell 1, cell 2, and cell 3 respectively, and found to remain constant for a longer time (in days) which indicates stability in open circuit conditions. The expected OCV of the system ~1.71 on the amount of standard oxidation and reduction potential of Zn (E^0_{oxi} = 0.76V) and V_2O_5 (E^0_{red} = 0.95V).

6.4.2 Discharge Characteristics

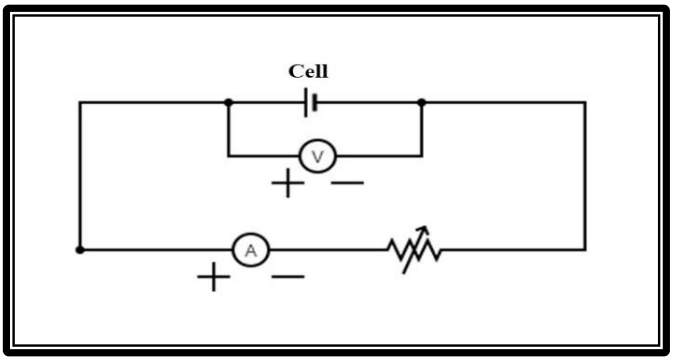


Figure 6.4 Discharge circuit for testing a cell via a constant load

The discharge characteristics are tested using the above discharge circuit (Figure 6.4) where at constant load, constant current drains from the cell.

All prepared cell was discharged at 4.8 KΩ, 10 KΩ, and 21 KΩ and cell potential was monitored as a function of time. Figures 6.5, 6.6, and 6.7 depict the discharge characteristics of cell 1, cell 2, cell 3. It is noticeable in the discharge curve, initially, there are drops in cell potential. This drop of voltage is due to possible active ohmic polarization of the anode and cathode material and/or development of passivation layer of Li^+ at the electrolyte - electrode surface. And thereafter cell potential remains near-constant for a particular time (min) for the different cells. This constant region with discharge time is referred to as the plateau region and corresponds to voltage as plateau voltage. And then abrupt decay in cell potential is observed as time increases. The initial decrease in the voltage due to polarisation or formation of ion layer near the electrodes.

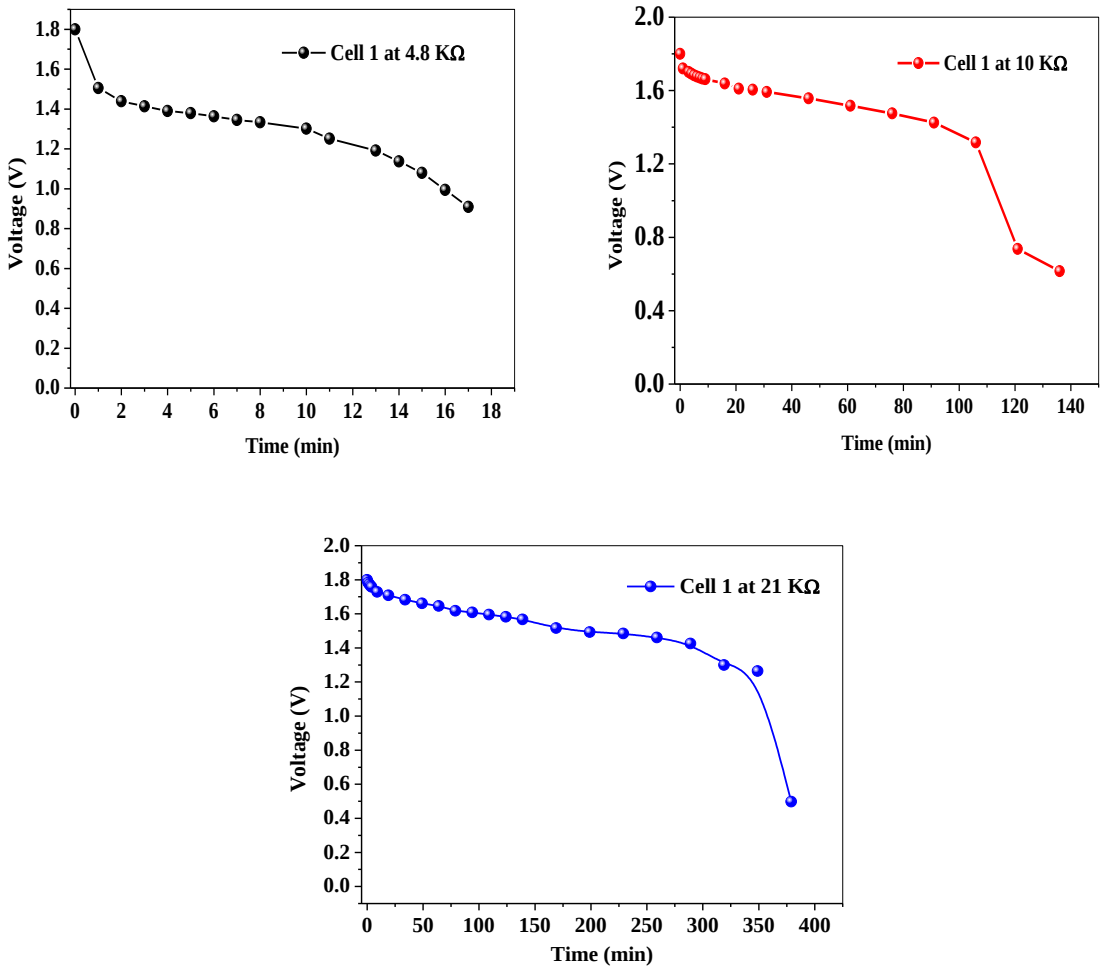


Figure 6.5 Discharge profile of cell 1 at 4.8 KΩ, 10 KΩ, and 21 KΩ

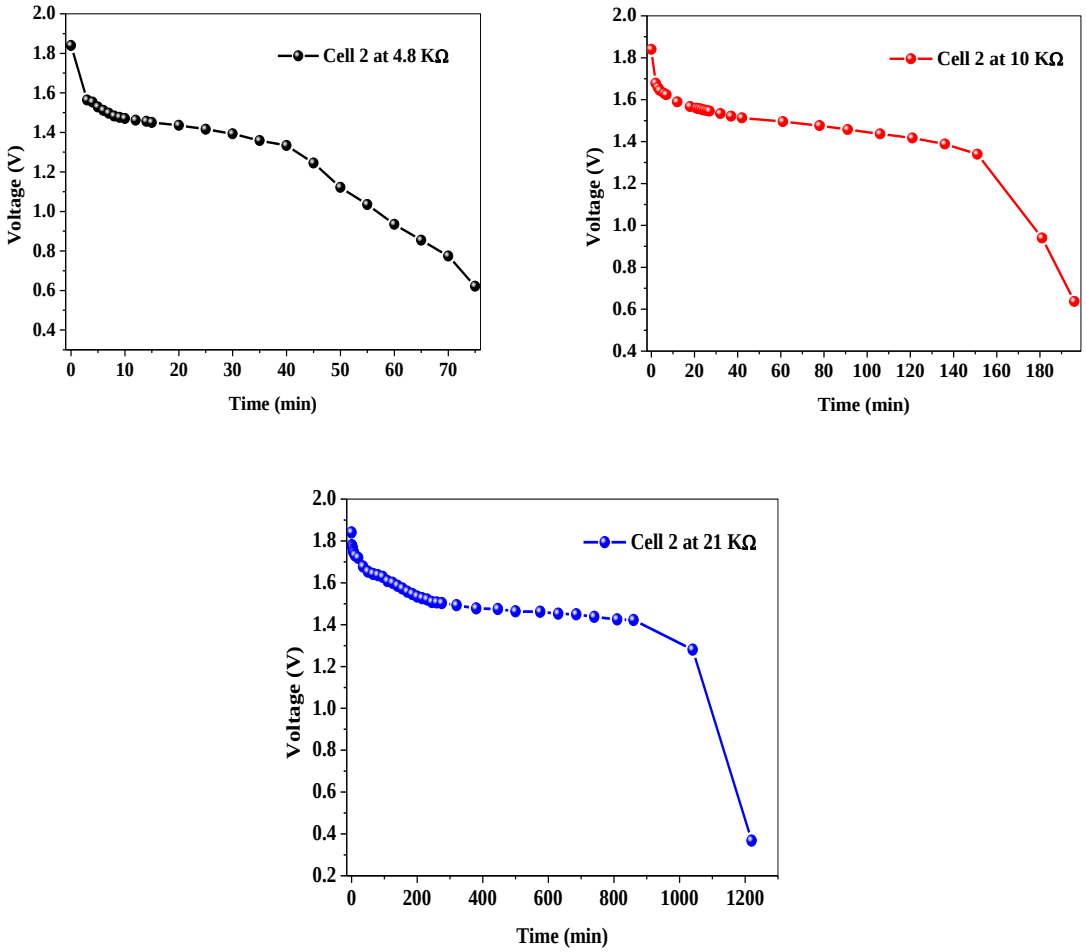
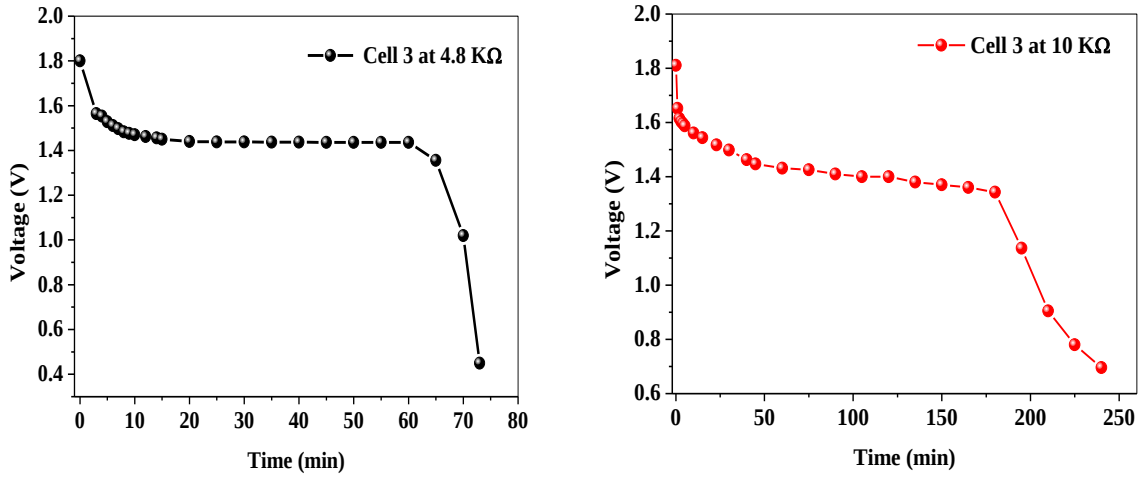


Figure 6.6 Discharge profile of cell 2 at 4.8 KΩ, 10 KΩ, and 21 KΩ



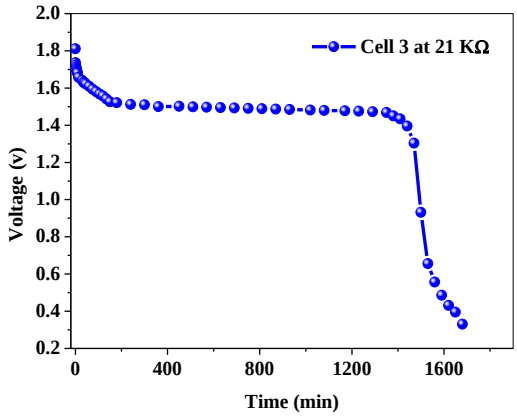


Figure 6.7 Discharge profile of cell 3 at 4.8 KΩ, 10 KΩ, and 21 KΩ

Table 6.2 Battery parameters from discharge characteristics

Cells	Load (KΩ)	Discharge time for plateau region (Hour)	Current density (μAcm^{-2})	Discharge capacity (μA h)	Specific power (mW/kg)	Specific energy (Wh/kg)
	4.8	0.183	48.52	11.78	85.99	0.015
Cell 1	10	1.76	41.45	96.80	63.70	0.11
	21	5.32	19.60	138.32	34.26	0.19
	4.8	0.75	195.98	195	356.94	0.27
Cell 2	10	2.5	113.82	377.50	214.44	0.53
	21	17.31	45.23	1038.6	85.21	1.48
	4.8	1	188.44	250	360	0.36
Cell 3	10	3	105.52	420	182.45	0.55
	21	23.98	45.22	1438.8	84.64	2.14

Following conclusions are made from the observed discharge curve.

The long-distance plateau region is observed for all cells as resistance increases from 4.8 KΩ to 21 KΩ indicate the ability of the present battery to provide the electrical energy from its charge to a fully discharged state. The stability of the cell depends on how much current is drained from the cell. At low resistance (R = 4.8 KΩ) more current is drained from the cell. Hence, a short discharge plateau region has been observed whereas at higher resistance

due to less current drain value the performance is higher. The parameters such as current density, discharge capacity, specific power, and specific energy are calculated from the discharge profile and tabulated in Table 6.2. The performance of all cells at a lower load value is not good due to the quick discharge of the cell. On comparison of stable performance at each load resistance, cell 3 is found to sustain for a longer time and the maximum discharge capacity and specific energy is obtained at higher load resistance i.e. 21 KΩ. However, slightly less value of current density and specific power is obtained as compared to cell 2 at load resistance of 21 KΩ. The maximum discharge capacity is observed for cell 3, might be due to matching the internal resistance of NCGPE with the applied load. Cell 3 can be used as a potential candidate in a solid-state battery.

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