Fabrication and Investigation of the Charge/Discharge Characteristics of Zinc/PVA-KOH/Carbon Cell

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Electrochemical properties of a zinc/polyvinyl alcohol-potassium hydroxide/carbon cell have been investigated. In this cell, PVA-KOH gel has been used as an electrolyte with PVA/KOH wt.% ratio of 60:40, while zinc and carbon rods served as electrodes. The cylindrical glass vessel of length 3.0 cm and of diameter 2.0 cm has been used as a cell compartment. The current–voltage characteristics and open circuit voltage–time, charge voltage/current–time and discharge voltage/current–time studies have been done. The open circuit voltage has been observed for 160 h. It has been found that the cell shows stability and is rechargeable, too.

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1. Introduction

The preparation and study of polymer electrolytes remain an area of frontier research and are influencing the modern and future technologies of solid state and electrochemical devices such as rechargeable batteries, fuel cells, supercapacitors, smart windows and transparent conductors, etc. [1-3]. This is mainly due to the low cost, ease of device fabrication, interesting electrical, optical, and electrochemical properties. Many potential applications of the electrolytes may be realized via modification of their conductivity and investigation of their electrochemical properties [4–7]. Extensive studies have been carried out of the effects of doping on the conductivity of polymer electrolytes [1, 4, 5, 8]. These polymer electrolytes exhibit maximum conductivity for a certain wt.% ratio of the dopant and polymer [4]. In order to enhance the conductivity of these polymer electrolytes, the host polymer is mixed with an inorganic salt or alkali and one or more plasticizers [4, 9].

The electrochemical studies of batteries employing alkaline solid polymer electrolytes (ASPEs) and alkaline polymer gel electrolytes are currently an important thrust of research. Over the years, a variety of batteries have been investigated using ASPEs but most of these studies have been based on polyethylene oxide (PEO) as a host polymer. A brief review of these studies is given in [10]. Yang and Lin reported a polyvinvyl alcohol-potassium hydroxide (PVA-KOH) polymer electrolyte for use in Ni–MH and Zn–air batteries [11, 12]. Ionic conductivity studies of PVA-KOH polymer electrolyte have been carried out by Mohammad et al. [4] for different wt.% ratio of PVA and KOH. This study has reported the highest room temperature conductivity of 8.5×10^{-4} S cm⁻¹ of the PVA-KOH alkaline solid polymer electrolyte system with PVA/KOH wt.% ratio of 60:40. The nickel–zinc cell was fabricated while employing this PVA-KOH ASPE system. Charge-discharge studies of this cell proved that a whole solid-state Ni–Zn cell can be prepared with the use of PVA-KOH solid polymer electrolyte.

Despite the fact that zinc-based batteries have been used around for a long time, various zinc-based systems have been under significant and increasing R&D activities in recent years [13]. This is largely due to the driving forces from the consumer electronics market, development of hybrid and electric vehicles and special applications including military applications [13]. In a recent study by Karimov et al. [1], the electrochemical behavior of Zn/orange dye aqueous solution/carbon cell has been investigated. In this cell, the aqueous solution of an organic semiconductor orange dye has been used as an electrolyte. The cell has been found to be rechargeable. The open-circuit voltage and short-circuit current of the fresh and fully charged cell have been reported to be 1.5 V and 0.45 mA, respectively. The discharge voltage/current-time characteristics of this cell exhibited stable and constant behavior. The voltage and current generated by an electrochemical cell is directly related to the types of materials used in electrodes and electrolyte.

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Therefore, we may expect better results from the Zn–C cell employing PVA-KOH gel polymer electrolyte with PVA/KOH wt.% ratio corresponding to maximum conductivity.

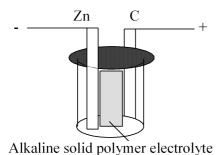
This paper reports the charge and discharge characteristics of Zn–C cell based on the PVA-KOH gel polymer electrolyte with PVA/KOH wt.% ratio of 60:40. Zinc– carbon cells are the most popular primary cells [14] but related literature shows that no study has been done on these cells employing PVA-KOH alkaline polymer electrolyte system.

2. Experimental

Polyvinyl alcohol (MERCK) of molecular weight 72,000 and KOH purchased from the local market were used for preparation of the alkaline polymer gel electrolyte for zinc/PVA-KOH/carbon electrochemical cell. The wt.% ratio of PVA and KOH in the polymer electrolyte gel, taken as a sample, was 60:40. At this ratio the PVA-KOH system exhibited the maximum conductivity [4].

In order to make PVA-based polymer electrolyte gel, 3.0 g of PVA was poured into 100 ml of distilled water in a 250 ml beaker and placed on hot plate at 80 °C. When PVA was fully dissolved in distilled water, 2.0 g of KOH was added and the porous alkaline polymer electrolyte gel was obtained.

Experimental cell assembly made of the polymer gel electrolyte-based zinc/carbon cell is shown in Fig. 1. The cell was sealed in cylindrical glass vessel and cell's length and diameter were 3.0 and 2.0 cm, respectively. Thickness of gel electrolyte layer employed between carbon and zinc electrodes was 1.0 cm whereas the length of both the electrodes was 4.0 cm and the volume of alkaline polymer electrolyte gel used was 4.0 cm^3 .



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Fig. 1. Schematic of the zinc/PVA-KOH/carbon cell.

The discharge voltage–current, open circuit voltage– time, charge voltage/current–time and discharge voltage/current–time characteristics of cell were measured at room temperature by Keithley 196 Digital Multimeter. For voltage versus current discharge characteristics (Fig. 2), the cell was connected with a variable resistor (load). A digital voltmeter was connected parallel to the load and ammeter in series

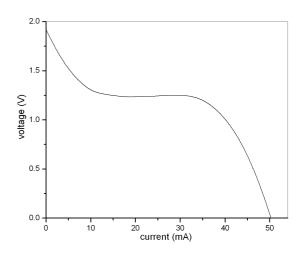


Fig. 2. Voltage versus current discharge characteristic of the zinc/PVA-KOH/carbon cell.

to the load. The open-circuit voltage was measured when the load was disconnected, and the short-circuit current was measured when load was short circuited. All other data points of voltage versus current discharge characteristics were obtained by measurement of voltage and current at different values of load. If the load resistance was small, the current increased and vice versa. The cell was charged at constant voltage as is used usually for charging of conventional rechargeable cells. Constant-voltage (often called constant-potential) chargers maintain nearly the same voltage input to the cell throughout the charging process, regardless of the cells' state of charge.

3. Results and discussion

Figure 2 shows the discharge voltage-current (V-I) relationship of zinc/PVA-KOH/carbon cell. The zinc electrode's potential has negative polarity with respect to the carbon electrode [1]. For electrochemical cells, the V-Irelationship is typical [15]. The values of open-circuit voltage and short-circuit current of fully charged cell are 1.919 V and 50.280 mA, respectively. The measured open-circuit voltage of this cell is 0.419 V larger than the zinc-carbon cell reported by Karimov et al. [1] and the short-circuit current of this cell is about 100 times larger than the value of short-circuit current reported in [1]. The large value of short-circuit current indicates that the polymer gel prepared from potassium hydroxide has high ionic conductivity.

The charging curves of the cell are shown in Fig. 3. It is found that the cell is rechargeable and attains saturated values of current and voltage during initial 40 min of charging. Figure 4 shows the discharging curves of the cell. The cell was discharged at a load of 100 Ω . Initially, the current drops very sharply and then becomes stable. This behavior could be due to the small value of the load resistor.

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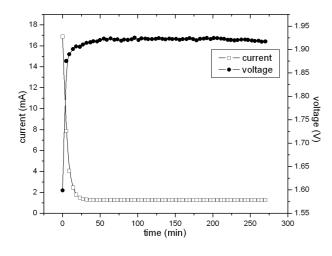


Fig. 3. Charge voltage/current–time curves for the zinc/PVA-KOH/carbon cell.

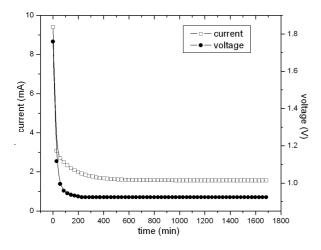


Fig. 4. Discharge voltage/current–time behavior for the zinc/PVA-KOH/carbon cell.

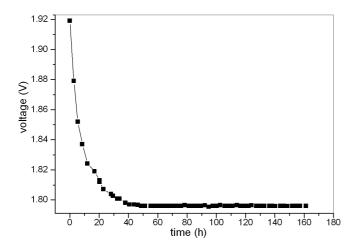


Fig. 5. Open-circuit voltage versus time of the zinc/PVA-KOH/carbon cell during 160 h of storage.

Figure 5 shows open-circuit voltage of the polymer gel electrolyte-based zinc/carbon cell during 160 h of storage. The cell was in the discharged mode, then again charged for four hours and the voltage of about 1.9 V was obtained. After charging, the open-circuit voltage was measured for 160 h. It can be seen from the plot that the open-circuit voltage of the cell drops to ≈ 1.8 V during first 23 h and then remains constant for next 137 h, which shows excellent stability of the cell.

The current efficiency (E_i) for a fixed time (t) of 3 h is 57% at 100 Ω load resistor as calculated by the following formula [16]:

$$E_i = \frac{\int_0^t I_\mathrm{d} \,\mathrm{d}t}{\int_0^t I_\mathrm{c} \,\mathrm{d}t},\tag{1}$$

where $I_{\rm d}$ is discharging current and $I_{\rm c}$ is charging current.

In the zinc/PVA-KOH/carbon cell, the zinc electrode was replaced by carbon and the cell was charged. It was found that in the discharge mode the operating voltage dropped from 182.7 to 15.3 mV and current decreased from 0.34 to 0.005 mA, during 12 h. This indicates that in the zinc/PVA-KOH/carbon cell, the zinc electrode was active with respect to that of carbon.

The electrical energy of the cell as a change of free energy (ΔG) was found to be -370 kJ mol^{-1} by using following expression [15]:

$$G = -nFE, \qquad (2)$$

where n is the number of electrons transferred per mole (it is equal to 2), F is the Faraday constant (96487 C), and E is the electromotive force (1.919 V) of the cell.

The capacity of the cell (C) was calculated by the expression [15]:

$$C = \frac{nFW}{MW},\tag{3}$$

where W is the weight of the active electrode material (zinc in this case) equal to 2.106 g whereas MW is the molecular weight of the material (for zinc it is equal to 65.37). The calculated value of the C is 6.22 kC = 1.72 A h.

4. Conclusions

The zinc–carbon cell has been assembled by employing alkaline polymer electrolyte gel and its electrochemical properties have been investigated and it has been concluded that the cell is rechargeable. The values of open-circuit voltage and short-circuit current of the fresh and fully charged cell have been observed as 1.919 V and 50.28 mA, respectively. Zinc/PVA-KOH/carbon cell exhibits good charge–discharge characteristics. The current discharge/charge efficiency is 57%. The stable and constant behavior was observed for discharge voltage/current–time characteristics and quick charging response was noted for this cell. The alkaline polymer gel electrolyte used in this study seems to have potential for the fabrication of secondary batteries.

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References

- Kh.S. Karimov, M.H. Sayyad, M. Ali, M.N. Khan, S.A. Moiz, K.B. Khan, H. Farah, Z.M. Karieva, J. Power Sources 155, 475 (2006).
- [2] A. Lewandowski, M. Zajder, E. Frackowiak, F. Begúin, *Electrochem. Acta* 46, 2777 (2001).
- [3] H. Pu, P. Huang, Mater. Lett. 60, 1724 (2006).
- [4] A.A. Mohammad, N.S. Mohamed, M.Z.A. Yahya, R. Othman, S. Ramesh, Y. Alias, A.K. Arof, Solid State Ionics 156, 171 (2003).
- [5] S. Rajendran, M. Sivakumar, R. Subadevi, J. Power Sources 124, 225 (2003).

- [6] G.M. Wu, S.J. Lin, C.C. Yang, J. Membrane Sci. 280, 802 (2006).
- [7] C. Iwakura, S. Nohara, N. Furukawa, H. Inoue, Solid State Ionics 148, 487 (2002).
- [8] Ch.V.S. Reddy, A.K. Sharm, V.V.R. Narasimha Rao, *Polymer* 47, 1318 (2006).
- [9] Ch.V.S. Reddy, A.K. Sharm, V.V.R. Narasimha Rao, *J. Power Sources* **111**, 357 (2002).
- [10] C.C. Yang, S.T. Hsu, W.C. Chien, J. Power Sources 152, 303 (2005).
- [11] C.C. Yang, S.J. Lin, Mater. Lett. 57, 873 (2002).
- [12] C.C. Yang, S.J. Lin, J. Appl. Electrochem. 33, 777 (2003).
- [13] S. Chandra, S.S. Sekhon, R. Srivastava, N. Arora, *Solid State Ionics* **154-155**, 609 (2002).
- [14] Z. Rogulski, A. Czerwiński, J. Power Sources 114, 176 (2003).
- [15] D.B. Hibbert, Introduction to Electrochemistry, Macmillan Press Ltd., London 1993, p. 294.
- [16] D.R. Crow, Principles and Applications of Electrochemistry, 3rd ed., Chapman and Hall, London 1988, p. 202.