Effect of temperature and charge stand on electrochemical performance of silver oxide–zinc cell

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ABSTRACT

It is known that the storage conditions influence the performance of a battery. The effect of temperature on the discharge capacity of silver oxide–zinc (AgO–Zn) cells is investigated quantitatively in the present study. 40 Ah silver oxide–zinc cells are charged in two step constant current mode up to 2.05 V and stored at temperatures in the range of −20 °C to 60 °C for charge stand periods of 1 day, 7 days and 15 days. Subsequently, the cells are discharged at 1 C rate current until voltages of each cell reached 1.2 V. Although the discharge capacity of these cells at and around room temperature is reasonable, at temperatures below 0 °C the performance is poor. From 40 °C to 60 °C temperatures, the discharge capacities decreased with charge stand periods. The discharge capacities are not affected by the charge stand periods from −20 °C to 30 °C. Best performances in terms of the capacity and average midpoint voltage for different charge stand periods are obtained at 30 °C. To identify the reasons for the poor performance at sub-ambient temperatures, electrochemical impedance studies are carried out on a fresh cell. The impedance data are analyzed using an equivalent circuit by Zman fitting software and the impedance parameters are evaluated. The resistances corresponding to mid-frequencies and low frequencies of Nyquist impedance plot exhibit a strong dependence on temperatures. The kinetic parameter namely, apparent exchange current density is calculated and discussed.

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1. Introduction

The rechargeable alkaline silver oxide–zinc batteries are noted for their high specific energy and power. During the initial stages of charge–discharge cycling they offer the highest power density, up to about 600 W kg^{-1} and energy density of 300 Wh kg^{-1}. Commercially available lithium-ion batteries offer less than 200 W kg^{-1} of power density and about 120–150 Wh kg^{-1} of energy density [1,2]. The AgO–Zn cells can operate efficiently at extremely high discharge rates and they exhibit good charge acceptance at moderate rates, and posses low self-discharge. Rates as high as 20 times the nominal capacity (20 C rate) can be obtained from specially designed silver–zinc batteries because of their low internal impedances. These high rates, however must often be limited in time duration because of potentially damaging temperature rise within the cells.

Although AgO–Zn battery is expensive due to its silver ingredient, it is a preferred power system for several critical applications in space programmes, underwater applications, etc.

One of the original applications for the silver–zinc battery is for use in torpedoes [3]. Short wet-life and low cycle-life (ranging from 10 up to 250 deep cycles, depending on design and use) decreased performance at low temperatures, sensitivity to overcharge and high cost are its serious limitations [4]. 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. The delivered capacity of the cell during discharge must still be high and all other performance criteria should be within acceptable limits. Further, when deployed in underwater vehicles, the batteries are exposed to different environmental conditions and require to retain 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. The calendar life of these batteries is short due to the degradation of the separator in alkaline conditions, but new separator materials are developed to offer stability [5–8]. Several studies are reported to improve the characteristics of the cell components [9]. Although there is a potential demand for AgO–Zn batteries for specific

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Nomenclature

C	Capacitance (F)
C_{dl}	Double layer capacitance (F)
CPE	Constant phase element (Ω^{-1})
F	Faraday constant (96,487 C mol^{-1})
f	a.c Frequency (Hz)
I_o	Exchange current (mA/cm^2)
L	Inductance (μH)
Q^*	Admittance (Ω^{-1})
Q_1	Constant phase element corresponds to high frequency semicircle (Ω^{-1})
Q_2	Constant phase element corresponds to low frequency semicircle (Ω^{-1})
M	Molarity (mol/L)
n	Phase change value obtained from fitting
R	Resistance (Ω) or universal gas constant (8.3143 J mol^{-1} K^{-1})
R_1	Resistance corresponds to high frequency semicircle (Ω)
R_2	Resistance corresponds to low frequency semicircle (Ω)
R_Ω	Ohmic resistance (Ω)
R_{ct}	Charge transfer resistance (Ω)
T	Temperature (°C)
ω	Angular frequency (rad/s)

applications, studies on characterization of these batteries are rarely reported [10].

A large number of AgO–Zn cells are subjected to prolonged periods of storage under various experimental conditions and impedance measurements are carried out at 40 Hz square-wave current [11]. The measured impedance is treated as a lumped parameter and it has not been separated into resistive and capacitive components in this study. The impedance characteristics of AgO–Zn cells are anticipated to be interesting as the composition of the positive electrode transforms from the semi-conducting AgO through the insulating Ag$_2$O to the metallic Ag during the course of discharge. The most important characteristic of this battery is that initially the impedance is very low but it can vary considerably with factors such as discharge current density, state-of-discharge, operational temperature, active material composition, cell ageing and cell size [12]. A physical description of the silver–zinc battery, with design specifications and calculations is provided by Himy [13]. A wealth of experimental information is available on the behavior of silver–zinc cells [14–18].

2. Experimental

AgO-Zn cells of 40 Ah capacity of $143 \times 80.5 \times 27$ mm ($H \times W \times T$) and a dry weight of 507 g were obtained from M/s HBL power systems Ltd., India. The cells are positive limited with thirteen positive (AgO) and fourteen negative (Zn) electrodes in each cell. 100 ml of 6 M KOH electrolyte was added and the electrodes were soaked for 72 h. The cells were conditioned by conducting a charge–discharge formation cycle. During the course of formation, the cells were charged at $C/20$ rate up to 2.05 V followed by discharge to 1.2 V at $C/10$ rate. In the present study, 27 nos. of above mentioned cells with similar mass, open circuit voltage, internal resistance and capacity at SOH = 100% were taken. Cells were divided into 9 groups, each group containing 3 nos. of cells. Constant current (CC) charging of cells was done using Power-tronics (60 V/10 A) DC power supply. The cells were charged at a CC of 3 A ($C/13.33$) until the voltage reached 2.0 V. Following this, a CC of 1 A ($C/40$) maintained until the voltage reached 2.05 V. On completion of charge, the cells were kept in the Enviro-Tech (-30 °C to 100 °C) climatic chamber immediately. Schematic diagram of experimental setup is shown in Fig. 1. The cells were stored at different temperatures between -20 °C and 60 °C in steps of 10 °C (i.e., -20, -10, 0, 10, 20, 30, 40, 50 and 60 °C). They were stored for durations of 1 day, 7 days and 15 days of charge stand periods inside the climatic chamber. The temperatures and charge stands (storage periods) at which the cells were tested are shown in Table 1.

On completion of respective time intervals, the cells stored at different temperatures were discharged at 40 A (1 C rate) current until the cell voltage reached 1.2 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 newly commissioned 40 Ah AgO–Zn cell using IVIUM Potentiostat/Galvanostat machine. Charging of this cell was carried as per above mentioned procedure. 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 and -20 °C) with 6 h equilibration time. Data acquisition and analysis were done using the Zman software.

3. Results and discussion

In a AgO–Zn cell, the electrode reactions are reversible in nature, even though the cycle-life is generally reported to be rather limited. However, longer cycle life has also been reported by suitable modifications of the cell design [19]. The reversible reaction is given below [20].

$$AgO + Zn + H_2O \underset{charge}{\overset{discharge}{\rightleftarrows}} Zn(OH)_2 + Ag \qquad (1)$$
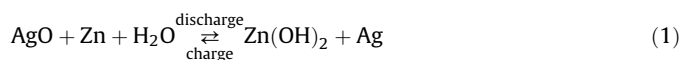
Zn/Zn(OH)$_2$ constitutes the redox couple at the negative electrode. The reaction mechanism involves the formation of super-saturated zincate solution by electron-transfer reaction [21]. From super-saturated zincate solution the formation of porous ZnO on the electrode surface takes place by chemical reaction. The redox couples that exist at the positive electrode are AgO/Ag$_2$O and Ag$_2$O/Ag. The reduction of AgO to Ag occurs in two stages. Whereas the redox reaction between AgO and Ag$_2$O occurs via a solid-state mechanism resulting in the formation of a solid solution of AgO–Ag$_2$O, the reaction between Ag$_2$O and Ag involves a dissolution–precipitation mechanism. The standard electrode potentials of these stages are distinctly different and the reactions also proceed with different mechanisms. The voltage of a AgO–Zn cell varies over a wide range, which depends largely on the positive electrode.

The variation of voltage of 40 Ah AgO–Zn cell under galvanostatic charge–discharge cycling at 8 A in the voltage limits between 2.05 and 1.2 V is shown in Fig. 2. During charge, there are two plateau regions at 1.65 and 1.95 V corresponding to the two stages of oxidation of the positive electrode. The voltage spike observed at the transition of the first and the second plateaus is due to highly resistive Ag$_2$O completely surrounding the electrode, as reported by Frank et al. [10]. The sharp rise corresponds to the time during charge when the layer of high resistance Ag$_2$O is completely