DISCHARGE CHARACTERISTIC OF SILVER SOLID STATE BATTERY

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ABSTRACT

DISCHARGE CHARACTERISTIC OF SILVER SOLID STATE BATTERY. A silver solid electrolyte based on superionic glass $(AgI)_x(AgPO_3)_{1-x}$ has been produced by melt-quenching method. The solid state batteries have been fabricated with the cell configuration: Anode//$(AgI)_x(AgPO_3)_{1-x}$//Cathode. Ag-metal was used as an anode, and Iodine was used as a cathode. The solid state battery discharge characteristic has been carried out under two different load conditions, 20 kΩ and 50 kΩ. Cell parameters viz. current density, power density, discharge capacity and energy density were evaluated and reported. The power density of the solid state battery was approximately larger than 3.45 mWh.

Key words : Solid electrolyte, solid state batteries, glassy electrolyte

ABSTRAK

KARAKTERISTIK PENGOSONGAN BATERAI PADAT PERAK. Elektrolit padat gelas superionik (AgI)x(AgPO3)1-x telah berhasil dibuat dengan metode pendinginan cepat. Selanjutnya elektrolit ini digunakan untuk membuat baterai padat dengan susunan: Anoda/(AgI)x(AgPO3)1-x/ Katoda. Logam Ag digunakan sebagai anoda, sedangkan bahan untuk katoda adalah I_2. Telah dilakukan pengujian karakterisitk pengosongan baterai padat tersebut degnan menggunakan beban tetap yang berupa hambatan listrik sebesar 20 kΩ dan 50 kΩ. Parameter baterai, seperti rapat arus, rapat daya, kapasitas pengosongan, dan rapat energi diukur dan dievaluasi hasilnya. Rapat daya dari baterai padat ini diperoleh lebih besar dari 3,45 mWh.

Kata kunci : Elektrolit padat, baterai padat, elektrolit gelas

INTRODUCTION

Everybody is familiar with the batteries that are used in a daily life. A battery is a device that converts the chemical energy contained in its active materials directly into electric energy by means of an electrochemical oxidation-reduction (redox). The type of reaction involves the transfer of electron from one material to another through an electric circuit. One cell battery consists of three major components, (1) The anode or negative electrode, (2) The cathode or positive electrode and (3) The electrolyte-the ionic conductor-which provides the medium for transfer of electrons, as ions, inside the cell between the anode and cathode [1].

For the most electrolytes in the market are typically liquid, such water or other solvents. The disadvantages of liquid electrolyte are leakage; need special handling and packaging, short lifetime and also will contaminate the equipments after being used. Due to this reasons, the researches on new solid electrolyte have been developed continuously for the last decade. Our group has concentrated on developing new solid electrolytes based on glassy material. We started from the family of phosphate-glasses with different glass modifier such as $AgPO_3$, $NaPO_3$, $CuPO_3$ and also $LiPO_3$. In order to increase the ionic conductivity at room temperature, a different doping salt, such as AgI, Ag_2S, AgBr or CuI were mixed together with the phosphate glass. New superionic glasses, such as AgI-$AgPO_3$, Ag_2S-$AgPO_3$, AgBr-$AgPO_3$, CuI-$AgPO_3$ and AgI-$NaPO_3$, were obtained [2-10]. Several characterizations have been performed on those glasses in order to understand their physical, thermal, electrical and structural properties.

The glass besides contains non-toxic and no-hazardous materials, it is also free from leakage, easy to be produced and formed as a thin film. Another important aspect, that this glassy material is safe and environmentally friendly. The glassy electrolyte must have good ionic conductivity but not be electrically conductive, as this would cause internal short-circuiting. For further application, a superionic glass AgI-$AgPO_3$ has been used as the solid electrolyte in a rechargeable battery [11-13].

Another important aspect on designing a battery is the combination of anode and cathode materials, which will determine the cell voltage and capacity. In practical system the anode is selected with the following properties: efficiency as a reducing agent, high coulombic output (Ah/g), good conductivity, stability, easy of fabrication, and low cost. Practically metals are mainly used as the anode material and the cathode must be an efficient oxidizing agent, be stable when contact with the electrolyte, and have a useful working voltage. The choice of cathode in most cases has to meet essential requirement. That is the potential difference between the cathode and anode must be high. Simultaneously, the solid electrolyte has to withstand this potential without decomposing the constituents.

For this solid state battery, we chose Ag/I_2 as the anode/cathode couple, because of several reasons. Silver metal was the obvious choice as an anode material because it is necessary to use a material of the same nature as the mobile ion in the electrolyte ($AgI\text{-}AgPO_3$) to assure uniform and continuous electrical charge transport through the three components of the battery. In this work, a coin type battery has been designed and fabricated, by sandwiching the three components of anode, electrolyte and cathode, respectively so the cell arrangement becomes $Ag/AgI\text{-}AgPO_3/I_2$. The diameter of battery is about 11.0 mm, and the thickness of about 3.5 mm (IEC standard). The cell has been inserted into an Aluminum casing, with the plastic used a separator. Two copper-disks were used as the current collector. To test the performance of the cell, a simple set of 'Discharge-system' has been designed and constructed. A simple test of the battery has been performed to characterize the battery performance.

THEORY

Cell Operation (Discharge and Charge)

The operation of a cell during discharge and discharge are shown schematically in Figures 1a and 1b. When the cell is connected to an external load, or during discharge, electrons flow from the anode, which oxidized, through the external load to the cathode, where the electrons are accepted and the cathode material is reduced. The electric circuit is completed in the electrolyte by the flow of anions (negative ions) and cations (positive ions) to the anode and cathode, respectively.

Discharge (Load)

The discharge reaction can be written, assuming a metal such as silver (Ag) as the anode material and cathode material such as Iodine (I_2), as follows :

Negative electrode (Anode) : anodic reaction

The oxidation or loss of electrons takes place at the anode with reaction

$$Ag \rightarrow Ag^{+} + e$$

Positive electrode (Cathode) : cathodic reaction

The reduction or gain of electrons takes place at the cathode with reaction

$$I_2 + 2e \rightarrow 2\,I^-$$

Overall reaction or discharge :

$$2Ag + I_2 \rightarrow 2Ag^{+} + 2\,I^- \,(2AgI)$$

The overall reaction is shown in Figure 1a. This is a discharge process. If this were a primary battery, at the end of discharge the device would be exhausted and discarded. However, Ag/I_2 cell is a secondary battery (rechargeable) system, therefore the cell can be recharged by returning electric energy to the device.

Charge

During the recharge of a rechargeable or storage battery, the current flow is reversed and oxidation takes place at the positive electrode and reduction at the negative electrode, as shown in Figure 1b. The positive electrode is now the Anode, where the oxidation takes place; while the negative electrode is now the cathode, where the reduction takes place. The electrons flow from the anode to the cathode.

In Ag/I_2 cell, the reaction on charge can be written as follows:

Negative electrode : cathodic reaction (reduction, gain of electrons)

$$Ag^{+} + e^{-} \rightarrow Ag$$

Positive electrode: anodic reaction (oxidation, loss of electrons)

$$2I^{-} \rightarrow I_2 + 2e^{-}$$

Overall reaction (discharge):

$$2Ag^{+} + 2I^{-}\,(AgI) \rightarrow 2Ag + I_2$$

After recharge, the secondary battery reverts to its original chemical state and is ready for further discharge. These are the fundamental principles involved in the charge-discharge mechanism of a typical secondary battery.

Theoretical Cell Voltage and Capacity

The theoretical voltage and capacity of a cell are a function of the anode and cathode materials. Theoretically, when a reaction occurs, there is a decrease of the free energy of the system, which is expressed by :

$$\Delta G^{o} = -\,n\,F\,E^{o}$$

where F = constant Faraday (~ 96.500 C or 26.8 Ah);
n = number of electrons;
E^{o} = standard potential, V

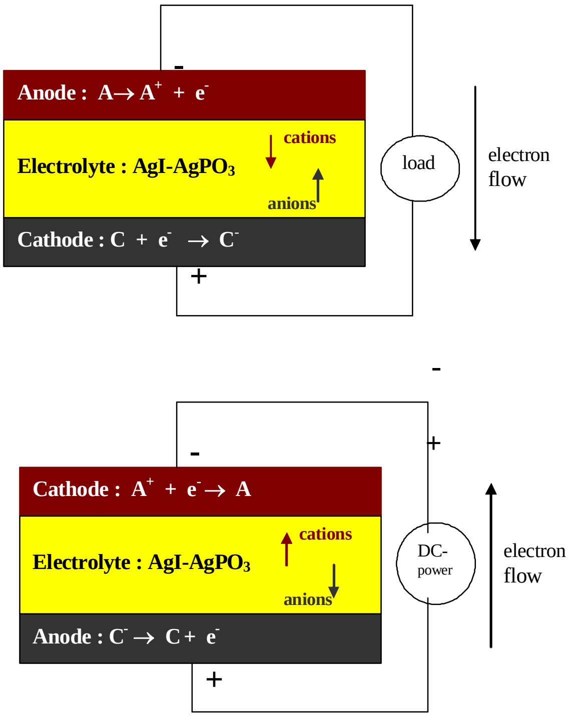

Figure 1. Electrochemical operation of a cell (a) discharge (b) charge.

Theoretical Voltage

The standard potential of the cell is determined by its active materials and can be calculated from free energy data or obtained experimentally. A listing of electrode potentials (reduction potentials) under standard conditions is given in Table 1.

Table 1. Standard reduction potential of electrode reactions at 25°C. [1]

Electrode reaction	Eo, V
$I_2 + 2e \Leftrightarrow 2I^-$	0.54
$Ag^+ + e \Leftrightarrow Ag$	0.80

The standard potential of a cell can be calculated from the standard electrode potentials as follows:

i). the oxidation potential is the negative value of the reduction potential

ii). standard cell potential = Anode (oxidation potential) + cathode (reduction potential) or $E^o_{cell} = E^o_{cathode} - E^o_{anode}$

For example, in the reaction

$$2Ag + I_2 \rightarrow 2Ag^+ + 2I^- \ (2AgI),$$
$$I_2 \rightarrow 2I^- - 2e$$
$$2Ag \rightarrow 2Ag^+ + 2e$$

$$2Ag + I_2 \rightarrow 2Ag^+ + 2I^- \ (2AgI)$$

The measured cell voltage for AgI is approximately 0.67 V, this is close to the calculated one. However, the cell voltage is also dependent on other factors, including concentration and temperature, as expressed by the *Nernst* equation. The cell's internal resistance IR will also lower the output voltage, where I and R are symbols for the current and resistance, respectively. All those factors, will affect the actual voltage condition that measured experimentally.

Theoretical Capacity

The capacity of a cell is expressed as the total quantity of electricity involved in the electrochemical reaction and is defined in terms of coulombs or ampere-hours. The "ampere-hour capacity" of a battery is directly associated with the quantity of electricity obtained from the active materials. Theoretically 1 gram-equivalent weight of material will deliver 96,487 C or 26.8 Ah. (A gram-equivalent weight is the atomic number or molecular weight of the active material in grams divided by the number of electrons involved in the reaction). The electrochemical equivalence of typical materials is listed in Table 2.

Table 2. Characteristic of Electrode Materials [1].

Anode(A)/ Cathode (C) Material	At.w or Mol. w (g)	Reduction potential at 25°C, (V)	Valence change	Density, (g/cm^3)	Electrochemical equivalents		
					Ah/g	g/Ah	Ah/cm^3
(A): Ag	107.8	0.80	1	10.5	0.248	4.02	2.60
(C): I_2	126.9	0.54	2		0.211	4.73	

The theoretical capacity of a battery system, based only on the active materials participating in the electrochemical reaction, is calculated from the equivalent weight of the reactants. Hence, the theoretical capacity of the Ag/I_2 system is 0.114 Ah/g, that is,

$$\begin{array}{ccccc} Ag & + & I_2 & \rightarrow & AgI \\ 4.02\ g/Ah & & 4.73\ g/Ah & = & 8.75\ g/Ah \text{ or } 0.114\ Ah/g \end{array}$$

Table 3. Theoretical voltage and capacity of selected Battery system

Battery	Anode	Cathode	Reaction mechanism	V	Capacity	
					g/Ah	Ah/kg
Silver/Iodide	Ag	I2	2Ag + I2 →2AgI	0.67	8.75	114

The capacity of batteries is also considered on an energy (watthour) basis by taking the voltage as well as the quantity of electricity into consideration,

Watthour (Wh) = Voltage (V) x Ampere-hour (Ah)

In the Ag/I_2 cell example, if the standard potential is taken as 0.67 V (ideal condition), the theoretical watthour capacity per gram of active material is

Watthour/gram capacity = 0.67 V x 0.114 Ah/g
= 0.076 Wh or 76 mWh

A common method for indicating the discharge as well as the charge current of a battery is the C rate, expressed as : $I = M \times Cn$, where I = discharge current (A); C= numerical value of rated capacity (Ah); n=C rate at which the cell battery was rated; M=multiple or fraction of C.

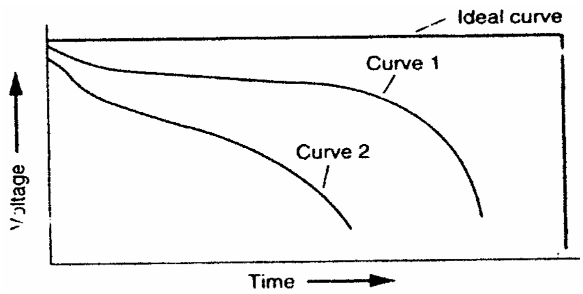

Figure 2a. Dicharging curve.

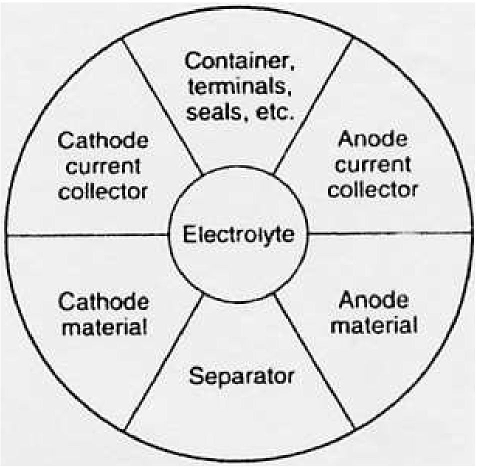

Figure 2b. Components of the cell.

Figure 2a shows the discharge plot of battery. In idealized case, the discharge proceeds at the theoretical voltage until the active materials are consumed and the capacity is fully utilized, then the voltage drop to zero. Under actual conditions, its voltage is lower than the theoretical voltage due to the presence of non reactive components (containers, separator, electrolyte) as illustrated in Figure 2b, and also to the *IR* losses of the cell resistance and polarization of the active material during discharge. The shape of the discharge curve can vary depending on the electrochemical system, constructional features and other discharge conditions.

EXPERIMENTAL METHOD

Preparation of Solid Electrolyte

The AgI-$AgPO_3$ was prepared by mixing appropriate amount of AgI, $AgNO_3$ and $NH_4H_2PO_4$ on a porcelain crucible. The mixture of raw materials then was heated gradually for 6 hours, and melted in a porcelain crucible to 500° C using an Ash furnace. The molten mixture was casted into a brass mould that has been quenched in liquid nitrogen. The sample preparation was done at Technology Center for Industrial Nuclear Materials, BATAN.

Battery Design

The design of the battery should include protective device and other features which can prevent, or at least minimize, the problem. There are two effects of cell design: (1) the constructional features of the cell strongly influence its performance characterization. (2) Electrode design, shape and configuration, volumetric efficiency versus energy density. Important factors on battery design, that affecting battery performance are cell uniformity, number of cells, series or parallel connections, battery case material and design, condition of discharge and charge, temperature.

In this research, we start designing a coin type battery with 1-cell arrangement configuration Ag/AgI-$AgPO_3$/I_2 . A small quantity of graphite or C,was mixed together with cathode to reduce the sublimation reaction. The dimension of the cell is 11 mm, diameter and 3.5 mm height. The Cu and plastic were used as a current collector and a separator, respectively.

Design and Fabrication of a Discharger System

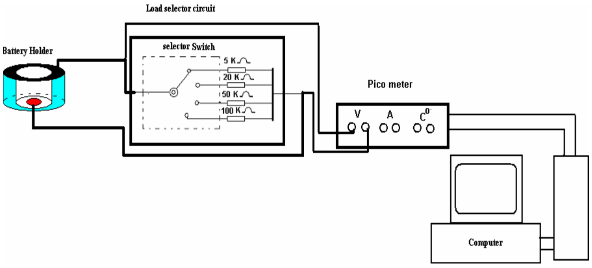

Figure 3. A set of discharger system to test performance of the battery.

In order to know performance of the battery during discharge, a set of discharger system has been designed and constructed. Figure 3 shows a design of a discharger system, that consists of battery holder, load selector, pico meter and computer. A battery holder is to put the battery during testing. The discharge was done by loading a battery via a resistor. In this equipment, four different resistances, such as 10k, 20k, 50k and 100kΩ can be chosen via a selector. The data of Voltage versus Time is automatically recorded via a pico meter and the measurement can be viewed online on the computer. Figure 4 shows a set of discharger equipment that has been constructed and used for testing the battery during discharge. This equipment has been used to test the battery as will be discussed in the following section.

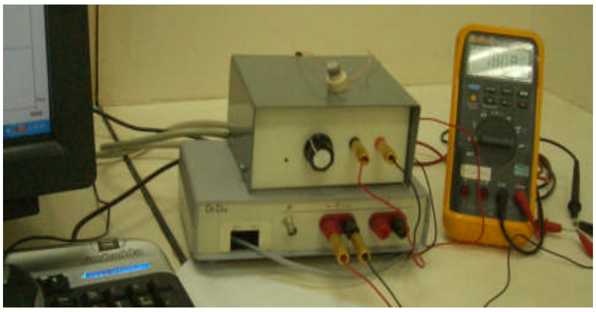

Figure 4. A set of discharger system for testing performance of the battery

RESULTS AND DISCUSSION

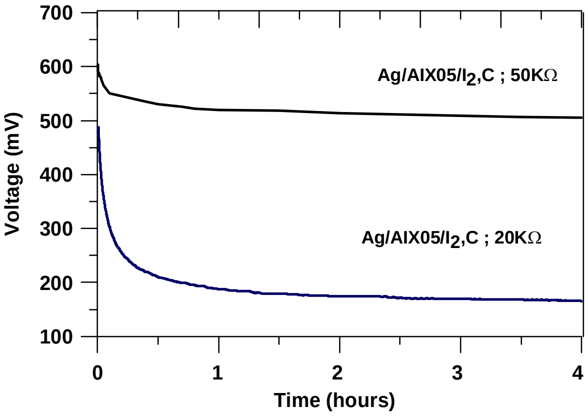

Figure 5. Discharge curve of coin type battery Ag/AgI-AgPO$_3$/I,C with different loads

The battery Ag/AgI-AgPO$_3$/I,C was discharged under different load, 50KΩ and 20KΩ. The battery gives an open circuit voltage 667 mVolt which is in a good agreement with the theoretical calculation. It is shown that the discharge curve for 20kΩ decreases slowly from 600 mVolt to 215 mVolt within 1 hour, then it stabilized at this voltage for 120 hours, before we stopped the program. A similar trend was observed for a battery which is being discharged by 50kΩ. The discharge curve decreases from 600 mVolt to 535 mVolt and it stays there for long hours. It is clear that the working voltage will be lower when the load given to the battery is larger, since it has the same capacity. In this experiment, unfortunately, we were unable to record the discharge curve until it becomes zero potential, since it last for more than 120 hours. The current drawn from the cell can be calculated from:

Current drawn = working voltage (V) / load (k)

the calculated current drawn are 10.75 and 10.70 A, respectively for 20 and 50 kΩ. The capacity of the battery can be calculated from how long the battery can be discharged at certain current until the voltage drops to zero. However, in this experiment as mentioned we only measured for 120 hours, though it is believed that the battery can still be discharged for longer time. For this measuring time, i.e. 120 hours, it will give the ampere-hour of about 1.3 mAh. Based on theory, that the capacity of battery is also considered on an energy (watthour) basis by taking the voltage as well as the quantity of electricity into consideration,

Watthour (Wh) = voltage (V) x ampere-hour (Ah)

If the working voltage is 0.535 Volt, the capacity of battery is about 0.69 mWh for 0.2 gr of active material or approximately is about 3.45 mWh for 1 gr of active material. Ideally from the theoretical calculation, the battery with Ag/I$_2$ will give 76 mWh. The capacity of our coin type battery is much smaller than the theoretical capacity, because of several reasons. In real condition, the coin type battery is affected by many factors, such as the separator, connector, casing, and also the electrolyte, which is not in ideal condition.

CONCLUSION

We have made a coin type battery based on glassy electrolyte with the cell arrangement Ag/AgI-AgPO$_3$/I$_2$. The open circuit voltage is around 0.667 volt which is in agreement with the theoretical calculation, but the working voltage is lower. For two different loads 50 kΩ and 20 kΩ, the working voltages are 535 mV and 215 mV, respectively. The calculated current drawn was about 10.7 μA and the capacity of the coin type battery is about 3.45 mWh, which is much smaller than the ideal battery. In the real condition, there are many factors affecting this capacity.

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