ISSN 1411-2213

TEST PERFORMANCE OF NEW IONIC CELL $Ag/(AgI)_{0.7}(AgPO_3)_{0.3}/I_2$

E.Kartini[1], A. Hindasyah[1], S. Purnama and Karvita[2]
[1] Research and Development Centre for Materials Science and Technology - BATAN
Kawasan Puspiptek, Serpong, Tangerang 15314
[2]Department of Physics, FMIPA - IPB
Jl. Raya Pajajaran Bogor 16144

ABSTRACT

TEST PERFORMANCE OF NEW IONIC CELL $Ag/(AgI)_{0.7}(AgPO_3)_{0.3}/I_2$. The demand for compact and high energy density batteries is constantly increasing with miniaturization of micro batteries and portable devices. All solid state batteries have attracted much attention, because of their potential for flexibility, safety and further miniaturization. In one ionic cell or cell-battery consist of two electrodes, a cathode and an anode, and a solid electrolyte. Superionic conductor has proved to be a good candidate for solid electrolyte. A new electrolyte based on silver-phosphate glasses AgI-$AgPO_3$ has been extensively studied by several different methods to observe the behavior of this material. However its performance as an ionic-cell is not well studied. In this paper we proposed a development of a new ionic cell $Ag/(AgI)_{0.7}(AgPO_3)_{0.3}/I_2$. An integrated system connected the cell, charge-discharge equipment, a Pico tech and computer has been built to display the cell performance. The result shows that the ionic cell works as a rechargeable battery, with the high trip voltage of 1.2 Volt and the output voltage can be adjusted from the input current.

Key words *:* Solid-state battery, superionic glass, ionic cell, rechargeable battery

ABSTRAK

UJI PERFORMAN PADA SEL IONIK BARU $Ag/(AgI)_{0.7}(AgPO_3)_{0.3}/I_2$. Kebutuhan akan baterai yang kompak dan memiliki kerapatan energi tinggi terus bertambah seiring dengan miniaturisasi dari baterai dan peralatan yang mudah dibawa. Semua baterai padat telah menarik perhatian, karena memiliki kelebihan yaitu bersifat fleksibel, aman dan dapat dibuat lebih kecil. Pada suatu sel ionik atau sel baterai terdiri dari dua elektroda, yaitu katoda dan anoda, dan sebuah padatan elektrolit. Konduktor superionik telah terbukti sebagai kandidat dari padatan elektrolit. Padatan elektrolit baru yang berbasis gelas perak-fosfat AgI-$AgPO_3$ telah dipelajari secara intensif dengan berbagai metoda untuk mengetahui berbagai sifat dari bahan tersebut. Namun performan daripada padatan elektrolit tersebut sebagai baterai belum banyak dipelajari. Pada makalah ini diusulkan untuk mengembangkan sel ionik baru $Ag/(AgI)_{0.7}(AgPO_3)_{0.3}/I_2$. Sebuah sistem yang terintegrasi yang menghubungkan sel, peralatan *charge-discharge*, sebuah *Picotech* dan computer telah dirancang untuk dapat men*display* performan daripada sel tersebut. Hasilnya menunjukkan bahwa sel ionik dapat bekerja sebagai baterai isi ulang, dengan batasan atas tegangan 1,2 Volt dan tegangan yang dihasilkan dapat diatur sesuai dengan arus masukan.

Kata kunci *:* Baterai padat, gelas superionik, sel ionik, baterai isi ulang.

INTRODUCTION

In the past, it was widely believed that the conventional batteries based on liquid electrolyte (typical examples being the lead acid and nickel cadmium or the high temperature Li/FeS_2 battery) have limited life period because of the corrosion reactions occurring between the liquid electrolyte and electrodes. Another problem is the leakage of the aqueous electrolyte from the battery which require special sealing or packaging techniques [1]. The requirement of miniaturized power sources for mounting the energy source on the electronic circuit board could not be met by these conventional aqueous electrolyte batteries [2]. Thus, the concept of an all solid state battery with the solid electrolyte attracted renewed interest every time a new solid electrolyte and new electrodes were invented. The solid state batteries are expected to have high energy density, wide range temperature of operation and long shelf life.

The solid electrolyte is a relatively new component in the all solid state battery compared to liquid electrolyte batteries. Some of the criteria for the solid electrolyte are (i) high ionic conductivity (ii) the transference number close to unity (iii) thermodynamically stable (iv) chemically and physically stable with the anode and cathode (v) processability as thin film for the miniaturization of the device. Some of those criteria were shown in superionic solid materials. Superionic solid is a solid electrolyte that characterized by high ionic conductivity $\sim 10^{-2}$ S/cm, compared with the well known ionic solid(e.g. NaCl, KCl~10^{-16} S/cm) [1]. However, many superionic solids exhibit such high ionic conductivity at high temperature for example crystalline AgI [3] and for the most appliances work at ambient temperature, therefore it was desired to obtain a superionic solid at room temperature, so that the electrolyte can be used in a solid state battery.

Due to these reasons, research effort on silver ion conducting solid electrolytes and silver solid state batteries was initiated at various institutions around the world [4-13]. One of the researchs was promoted to modify the already existing structure AgI to obtain a better conductivity by mixing AgI with another second component like polymer, ceramic, crystal or glass. Silver ion conducting glasses $AgI\text{-}AgPO_3$ were prepared by rapidly quenching the melt of different mole % $AgI\text{-}Ag_2O\text{-}P_2O_5$, where Ag_2O is a glass modifier to the glass forming oxides P_2O_5. The combination of Ag_2O with P_2O_5 yields a colorless transparent silver phosphate glass $AgPO_3$. At ambient temperature $AgPO_3$ shows low ionic conductivity (~ 10^{-7} S/cm), but the mixture of $AgI\text{-}AgPO_3$ shows the conductivity increase by few orders of magnitudes with increasing AgI and temperature as shown in Figure 1 [4].

The superionic glasses $AgI\text{-}AgPO_3$ have been extensively studied by many researchers around the

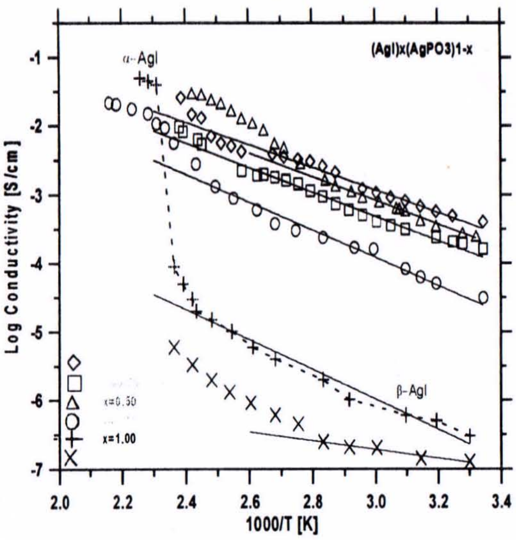

Figure 1. The ionic conductivity of the $(AgI)_x(AgPO_3)_{1-x}$ as a function of temperature and composition (x) [4].

world, to characterize the microscopic and macroscopic properties of the material [4-7,9-12]. However, the application of the superionic glass $AgI\text{-}AgPO_3$ as a solid electrolyte in an ionic cell is not well studied. In this paper we propose to develop a new ionic cell $Ag/(AgI)_{0.7}(AgPO_3)_{0.3}/I_2$ and to characterize its performance as a solid-state rechargeable battery. In this first test, we selected only one composition x = 0.7 as it shows the highest conductivity ~10^{-3} S/cm compared with other compositions.

EXPERIMENTAL

A superionic glass of $(AgI)_{0.7}(AgPO_3)_{0.3}$ composition was prepared at the Advanced Material Division, R&D Center for Material Science and Technology, BATAN. The glass was prepared as described elsewhere [6] by melting the mixture. For the AgI doped glasses, mixtures of ground AgI (purity 99.9%, Aldrich. Co), $AgNO_3$ and $NH_4H_2PO_4$ were heated gradually up to 600° C for about 6 hours. The molten mixture then was casted and subsequent quenched into cylindrical Brass that cooled by liquid nitrogen. A yellow transparent glass was obtained for $(AgI)_{0.7}(AgPO_3)_{0.3}$. The quality of the sample was measured by x-ray diffraction and the pattern showed broad peak with some precipitates correspond to AgI. This means that the sample is above the solubility limit (x>0.55) and $(AgI)_{0.7}(AgPO_3)_{0.3}$ becomes the superionic composite-glass [4].

The ionic cell based on superionic glass was fabricated with silver anode and iodine cathode. The ionic cell consists of $Ag/(AgI)_{0.7}(AgPO_3)_{0.3}/I_2$. The powders of solid electrolyte, cathode and anode were

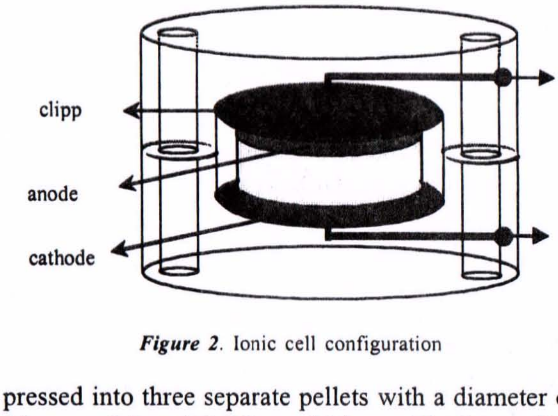

Figure 2. Ionic cell configuration

pressed into three separate pellets with a diameter of 15 mm and about 2.0-2.3 mm thickness. The three pellets were combined together as a sandwich with the solid electrolyte in the middle and the cathode and anode on both sides. The ionic cell configuration of the system is shown in Figure 2. No special cover was made in this experimental set up, the cell was simply connected to the charge-discharge system, as shown in Figure 3. A Pico Tech is connected to both charge-discharge equipment and computer to read and display the data, respectively [14].

RESULTS AND DISCUSSION

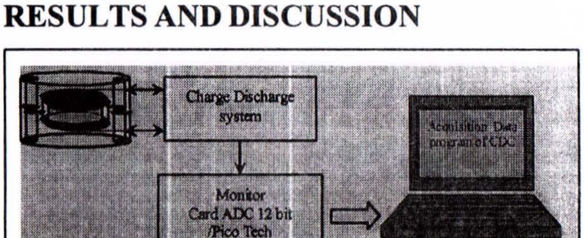

Figure 3. A set charge discharge measurement system

 ISSN 1411-2213

In our experiment, we used the ionic cell $Ag/(AgI)_{0.7}(AgPO_3)_{0.3}/I_2$ and anode/cathode couple Ag/I_2 for this solid state battery, 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 to assure uniform and continuous electrical charge transport through the three components of the battery. The choice of cathode in most cases happened to meet essential requirement that, the potential difference between the cathode and anode must be high. Simultaneously, the solid electrolyte has to withstand this potential without decomposing the constituents. Thus the anode/cathode couple was chosen Ag/I_2 for this silver solid state battery.

Figure 4 shows the first test result of the new ionic cell. The high trip Voltage was set at about 1.2 Volt and the low trip Voltage was 0.1 Volt. The charge-discharge current was set at about 13 μA. The Pico program was set to measure the data per mSec for 5000 cycles. Figure 4 shows how the ionic cell $Ag/(AgI)_{0.7}(AgPO_3)_{0.3}/I_2$ works automatically during charge and discharge. In a typical cell reaction, the $(AgI)_{0.7}(AgPO_3)_{0.3}$ electrolyte retains iodine during charge and release during discharge. The cell reaction is $Ag + 1/2I_2 \rightarrow AgI$, which is similar to the cell reaction of $Ag/AgI/I_2$ that has an open circuit Voltage (OCV) of 0.7 Volts [15]. During charging, the output Voltage increases within few hundred seconds to the higher trip Voltage 1.2 Volt, then it decreases again to the minimum Voltage value 0.1 Volt while it is being discharged. It took about 50 seconds for one cycle of charging and discharging, and the cycles were repeated for few thousands times for about 3 hours, before the measurement was stopped as shown in Figure 5. These cycles show the shelf life time of this ionic cell. This battery can flash the current density of about 5-10 μ/cm^2 of the anode, and has low capacity. One of the problems of this ionic cell is the used of I_2 as a cathode. This material sublimates at room temperature, and reduces the capacity for the cell to keep its reaction. To prevent iodine reaction it is suggested to use the graphite (C) so that the anode/cathode couple becomes

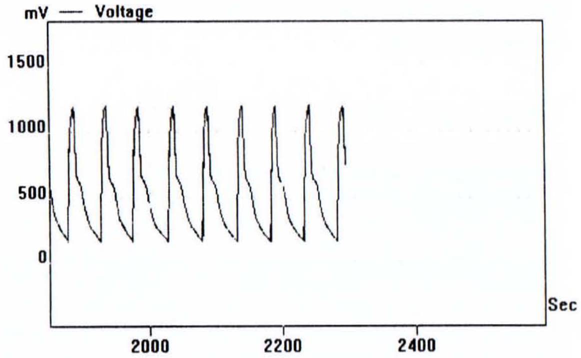

Figure 4. First charge-discharge result of ionic cell $Ag/AgI\text{-}AgPO_3/I_2$

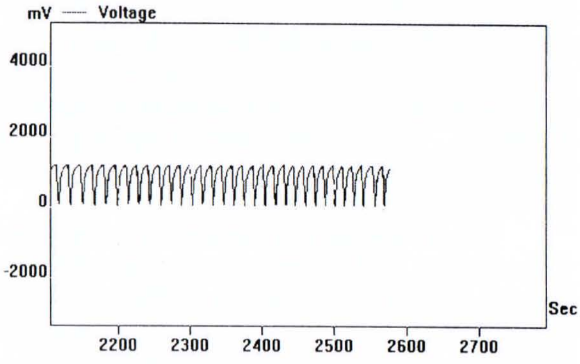

Figure 5. The charge-discharge cycles of ionic cell after 2600 sec.

$Ag/I_2,C$ as has been used by Takahashi et al. [16] on the ionic cell $Ag/Ag_3SI/I_2,C$ that can deliver over one mA/cm^2 at room temperature. The combination of this anode/cathode couple has not been used in the present study.

To know what was the maximum Voltage can be achieved for a given current, another set of test was made by changing the input current or charge current. In this case, the high trip Voltage was off, and the output was limited automatically by the input current. Figure 6 shows the plot of saturation of the ionic cell as a function of given current. For a given current i.e. 10 μA, the plot shows an increase of the output Voltage for a certain period and reaches a maximum value of 1.4 Volt before saturation, then it stays for a longer time in this limiting value. This means that the ionic cell has been saturated on a certain Voltage by a certain given current, or equally means that the output Voltage can be adjusted from the given current. The highest limit of the output that can be achieved or the maximum current can be accepted in the cell, will show how good the performance of the ionic cell. Figure 6 shows the performance of this cell, where the limited Voltages of 1.2 Volt, 1.4 Volt and 1.6 Volt can be reached for the given currents 4 μA, 10 μA and 20 μA, respectively. In this test, the maximum Voltage of 4 Volt was achieved for the given current 70 μA as shown in Figure 7. However, since the capability of the PicoTech is only up to 5 Volt, therefore we could not measure the data beyond this limit.

CONCLUSIONS

We have developed a new ionic cell based on the amorphous solid electrolyte or superionic glass $(AgI)_{0.7}(AgPO_3)_{0.3}$. Though extensive works have been performed on studying the macroscopic and microscopic properties of this glass, but its performance as the ionic cell $Ag/(AgI)_{0.7}(AgPO_3)_{0.3}/I_2$ was first studied. The system that consists of $Ag/(AgI)_{0.7}(AgPO_3)_{0.3}/I_2$ shows the ability as a rechargeable solid state battery, though the performance is not optimum. The output Voltage also really depends

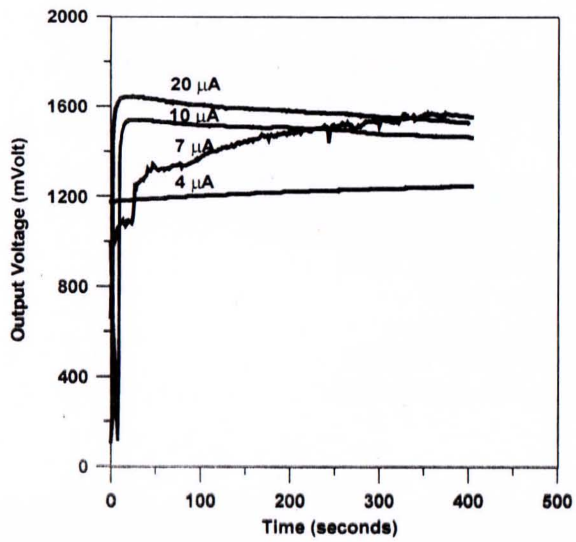

Figure 6. The saturation plot of ionic cell $Ag/(AgI)_{0.7}(AgPO_3)_{0.3}/I_2$ as a function of given-current.

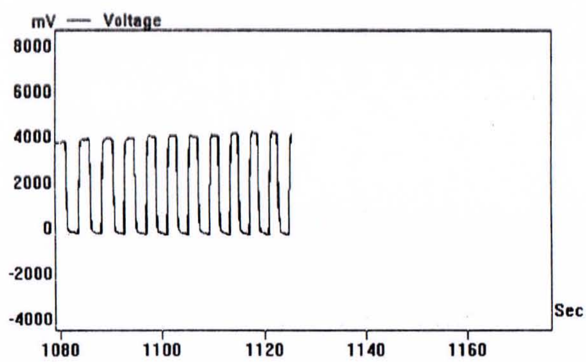

Figure 7. Charge-Discharge measurements for the input current 70 mA with the output voltage 4 Volt.

on the given current, and based on the experiment it achieves the maximum value of 4 Volt for the given current 70 μA. Further improvement of the ionic cell, as a dimension, packaging, pressing all the sample together, sealing and also finding suitable electrodes are necessary to be studied to obtain a better performance of this solid state battery. However, it is believed that this cell can be used a good solid state battery in the near future, with several advantages such as environmentally friendly, easy to be produced and shaped, also the has capability to be made as thin film for the micro battery.

ACKNOWLEDGEMENT

The authors acknowledged the Director of R&D Center for Materials Science and Technology, Heads of the Advanced Material Division and the Instrumentation Division for the opportunity given and facilities provided for this research. This work is supported through Batan Project (DIP 2003-2004).

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