

SYNTHESIS AND CHARACTERIZATION OF A NEW ELECTRODE MATERIAL : IODINE + VINYL PYRIDINE (I₂ + VP)

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF A NEW ELECTRODE MATERIAL : IODINE + VINYL PYRIDINE (I₂ + VP). Iodine is one of the electrode materials in a silver solid state battery. However, a serious problem is still found when it is used as an electrode in a battery system because iodine is a very reactive element and will react with water vapor which ionizes it to form I⁻. This ion then combines with I₂ to become I₃⁻ which has dark brown colour and it is very corrosive material. From the engineering point of view, it is very difficult to isolate the iodine electrode from the room atmosphere although an aluminum casing is used. The use of mixed iodine-vinyl pyridine (I₂-VP) was researched. The mixed iodine-vinyl pyridine was no longer reactive those from the EDAX results show that the iodine is still available in the mixed iodine- vinyl pyridine powder (more than 95 %). The total electronics and ionic conductivity of the mixed iodine- vinyl pyridine powder was measured by LCR meter and found that value of 3 S/cm at low frequency. However, the OCV of one cell battery (silver/electrolyte/I₂-VP) was only 0.1 volt.

Key words : Iodine-vinyl pyridine electrode, open circuit voltage

ABSTRAK

SINTESIS DAN KARAKTERISASI BAHAN ELEKTRODA BARU : YODIUM + VINIL PIRIDIN (I₂ + VP). Yodium merupakan salah satu bahan elektroda yang digunakan pada baterai padat perak. Namun demikian pada penggunaannya terdapat masalah yang cukup serius karena yodium adalah merupakan bahan yang sangat reaktif dan akan cepat bereaksi dengan air yang berada dalam udara sehingga terbentuk ion I⁻. Ion ini akan berkombinasi dengan I₂ dan menjadi I₃⁻ yang berwarna coklat tua dan mengakibatkan bahan logam menjadi sangat korosif. Secara teknis, elektroda yodium tidak mudah diisolasi terhadap udara walaupun sel baterai sudah dibungkus dengan aluminium. Untuk memecahkan masalah ini dilakukan penelitian untuk mencampur yodium dengan vinil piridin. Dari hasil penelitian diperoleh bahwa bahan campuran ini tidak lagi reaktif dan dari hasil pengamatan dengan menggunakan EDAX ternyata yodium masih terdapat dalam serbuk campuran (>95%). Setelah itu dilakukan pengukuran konduktivitas total (elektronik + ionik) dan diperoleh harga pengukuran sebesar 3 S/cm pada frekuensi rendah. Bahan elektroda baru ini selanjutnya digunakan untuk membuat sel baterai (perak/elektrolit/I₂-VP) dan diperoleh harga OCV sebesar 0,1 volt.

Kata kunci : Iodine-vinyl pyridine electrode, open circuit voltage

INTRODUCTION

The research of solid superionic electrolyte based on phosphate glass has been conducted in our group [1,2]. The glass based electrolyte(AgI)_x(AgPO₃)_{1-x} was made of AgPO₃ which was doped by using AgI. The characteristics of the electrolyte such as the electrical, thermal, and structure properties have been analyzed by using many different methods i.e. X-ray diffractometer, impedance spectroscopy, a DSC, and SEM and the results have been published elsewhere [3]. In order to prove that the electrolyte could be used as one of the element of a solid state battery, a one cell solid battery system that used (AgI)_{0.5}(AgPO₃)_{0.5} electrolyte, Ag and I₂ electrodes was made. Its charge-discharge characteristics has also been

reported [4]. In general AgI-AgPO₃ superionic glass has very high conductivity (~ 10⁻³ S/cm) compared with the un-doped AgPO₃ glass (~ 10⁻⁷ S/cm). Therefore the superionic glass can be used as an electrolyte in the solid state battery.

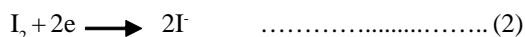
It is well known that iodine is a very reactive element. It has the electronegativity value of 2.2 [5]. Due to this value it tends to gain electrons from other substances and becomes oxidizing agent. From the engineering point of view, it is very difficult to isolate the iodine electrode from the room atmosphere although an aluminum casing is used. However, there is still a problem especially when pure iodine when it is used as the electrode in the battery. The battery elements such

as battery casing and Cu current collector will be corroded easily and the iodine will come out from the casing. Some efforts have been conducted such by molding the battery cell with resin and adding the iodine with carbon [4]. From the battery function the first effort can solve the problem but the fabrication become more difficult and the size is larger. The second effort could minimize the reaction of the iodine with water vapor but the corrosion still happens. The idea of exploiting polymer in the solid state battery was primary done by Chiang [6] who used polyacetylene as an electrode in the polymer battery.

In this paper we will present a preliminary study of using 4-vinyl pyridine for protecting electrode from sublimation. The new mixed iodine-vinyl pyridine ($I_2 + VP$) was then characterized by using X-ray diffractometer (XRD), impedance spectroscopy and Scanning Electron Microscope (SEM) in order to study its structural, electrical, and microstructural properties. Furthermore the new material $I_2 + VP$ will be used as an electrode in the solid state battery.

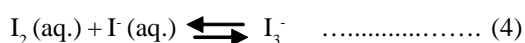
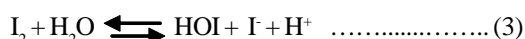
THEORY

I_2 powder can be used as an electrode in a battery system. At room temperature iodine forms dark metallic-looking crystals that easily sublime to give a purple vapor. It is known well that iodine has high chemical reactivity which is one of the characteristics of halogen substances in general, although its electronegativity is the smallest among the halogen substances. Due to the reason, iodine tends to gain electrons from other substances and it serves as an oxidizing agent. This property makes the I_2 can be used as a cathode material in the cell battery. In the silver solid state battery i.e. $AgI-AgPO_3$, $AgRbI-AgPO_3$, the electrode couple Ag/I_2 is commonly used. This is due to the reversible reaction as follows :



Where both agents can work either as an oxidant or reductant, when they are used in a cell battery $Ag/electrolyte/I_2$, the battery is rechargeable.

When iodine is used as an electrode of a battery, it is exposed to room atmosphere. Soon after being put in the room environment the iodine will react with water vapor. The following reaction occurs :



I_3^- has dark brown colour and it is very corrosive material.

To prevent the iodine from proceeding the above reaction, it can be mixed with 4-vinyl pyridine. In electronic configuration, the nitrogen of vinyl pyridine

is bonded to the other members of the ring by the use of sp^2 orbitals, and provides one electron for the π cloud. The third sp^2 orbital of nitrogen simply contains of a pair of electrons, which are available for sharing with acids or halogen molecules in the form of a coordinate covalent bond [5,7].



EXPERIMENTAL METHOD

I_2 -VP samples were made by mixing I_2 granular with liquid vinyl- pyridine with the ratio of 2 : 1. After being mixed the samples then being exposed in the room environment for about 24 hours. During the time, the samples became dry and were ready to be formed into coin type samples. Firstly, I_2+VP granule was ground by using a ceramic mortar, poured into a permanent dies, and pressed using the pressure of 200 kg/cm². Three coin type samples were made. The first sample was tested using SEM (Scanning Electron Microscope), and the second sample was measured by XRD to observe the structure of the material, both experiments were performed at PTBIN, BATAN. The third sample was measured its total ionic and electronic conductivity by using LCR meter HIOKI 3522-50 (BPPT).

RESULTS AND DISCUSSION

The results of the measurement by using SEM are shown in Figure 1 and Table 1.



Figure 1. SEM of the surface of Iodine-vinyl pyridine sample

The purpose of doing the experiment is to prove that after being mixed with vinyl-pyridine, the iodine is still available in the sample. The data written in Table 1. were taken in the two different positions (pointed by the arrows shown in Figure 1) and scanned for the whole positions shown in Figure 1. It is shown in Table 1 that the composition of the iodine is more than 95 % so it

Table 1. The results of the measurements of the sample's composition using EDAX

Measurement Position	I_2 (%)	Cr (%)	Fe (%)
Average over whole of the picture	95.92	1.17	2.91
First Position (see white arrow at the picture)	97.85	0.69	1.46
Second Position (see the black arrow at the picture)	98.96	0.35	0.69

means that the iodine is still available in the sample. The question is that whether the iodine is still in the form of I_2 molecules or it reacts with vinyl pyridine to make a new molecule.

To answer the above question we made other experiment using X-ray diffractometer (XRD). Two samples were irradiated and the diffracted beam was measured. The scanning time was 30 minutes. The pure iodine was used as the first sample and the X-ray pattern is shown in Figure 2.

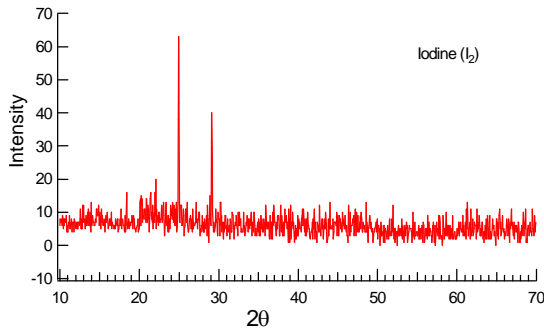


Figure 2. The X-ray diffraction pattern of pure iodine sample

Figure 2 shows that the pure iodine is in the form of crystalline structure. Two dominant peaks are shown in the Figure 2. The second coin type $I_2 + VP$ sample was irradiated by using X-ray of XRD within one hour to measure the diffraction pattern. The diffraction pattern of this sample is shown in Figure 3. From the pattern we can explore the information that the iodine crystalline is not available anymore because it has made a coordinate covalent bond as shown in the equation (5).

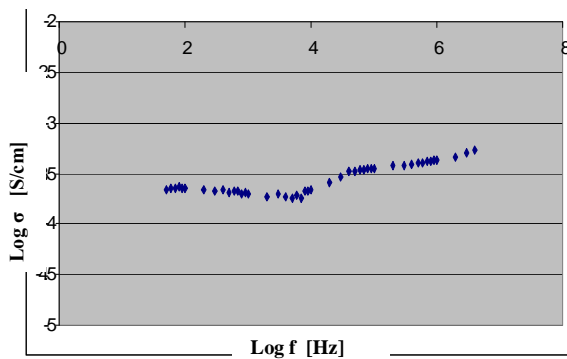


Figure 3. The diffraction pattern of I_2 -VP sample

For making sure that the I_2 is no longer available as free molecules, the $I_2 + VP$ powder was tested using *Benedict's* test. I_2 -VP powder was poured in starch solution (white) and there was no change in colour. This is in contrary if we add crystalline iodine into starch solution which changes the solution into blue colour.

The total electronic and ionic conductivity of I_2 -VP sample was measured using LCR meter. The results of the measurements are shown in the Figure 4.

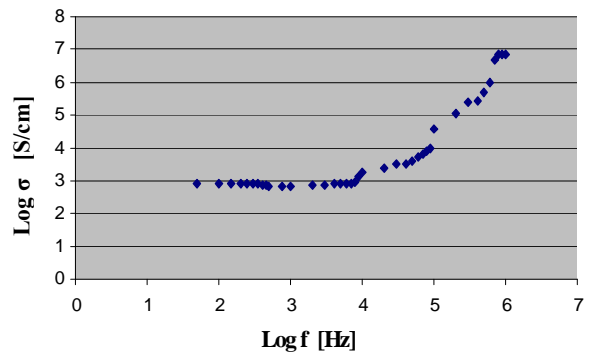


Figure 4. Total electronic and ionic conductivity of I_2 -VP sample

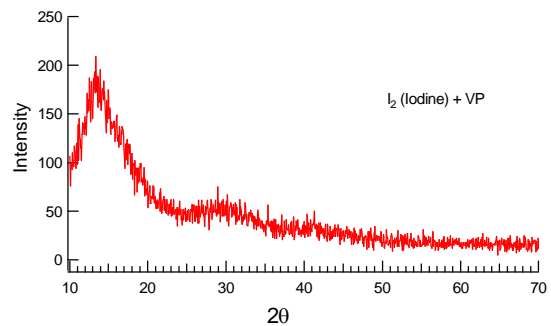


Figure 5. Total electronic and ionic conductivity of electrolyte glass of $(AgI)_{0.7}(AgPO_3)_{0.3}$ [8]

Compared with the electrolyte, the conductivity of an electrode is much larger (Figure 5). An electrolyte is an element of a battery which only conducts ions (cations and anions). The electrons are not allowed to pass through the electrolyte. On the other hand, an electrode should have 50% : 50% of electronic and ionic conductivity ratio. The requirement is needed because an electrode should conduct both electrons and ions in the same time. From Figure 4, it can be seen that the conductivity of $I_2 + VP$ sample is about 3 S/cm in the DC (direct current or low frequency region). The conductivity is exponentially increasing in the region of the frequency more than about 4 kHz.

By using this new electrode, a cell battery was made and a measurement of its open circuit voltage (OCV) is 0.1 volt. This value is still far bellow the theoretical value i.e. about 0.66 volt [9]. Further experiments should be performed to obtained the best composition of I_2 -VP, so that a higher OCV which is near the theoretical value can be reached. In order to improve the new electrode, the use of polyvinyl pyridine will also be explored.

CONCLUSIONS

Iodine is one of the electrode materials in a silver battery system. It has some drawbacks however, such as it sublimes easily and gains electrons from other materials. By mixing with vinyl pyridine the problems can be eliminated. Some experiments have been done for exploring its characteristics using SEM, XRD, Benedict's test, and LCR meter. By using SEM, XRD, Benedict's test, it was proved that the I₂-VP makes covalent coordination bond. By using the LCR meter the total electronics and ionic conductivity was measured and it is about 3 S/cm in the low frequency range. A cell battery (Ag/electrolyte/ I₂+VP) was also made. The OCV is 0.1 volt.

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