

DEVELOPMENT OF NEW NANO COMPOSITE ELECTROLYTE Ag/AgI/Ag BY PVD TECHNIQUE

E.Kartini¹, S. Nikmatin², S. Suminta¹ and A. Handayani¹

¹R&D Center for Materials Science and Technology, BATAN

Kawasan Puspiptek Serpong, Tangerang 15314

² Graduate Program for Material Science, University of Indonesia

Jl. Salemba 4, Jakarta

ABSTRACT

DEVELOPMENT OF NEW NANO COMPOSITE ELECTROLYTE Ag/AgI/Ag BY PVD TECHNIQUE. A new composite electrolyte Ag/AgI/Ag has been developed by a Physical vapour deposition (PVD) technique. Ag have been deposited on both sides of the coin type- superionic conductor AgI with deposition times 30, 45 and 60 minutes. Several characterizations on deposited Ag/AgI/Ag such as the crystal structure, micro structure, hardness, density, and ionic conductivity have been performed by using respectively, an X-ray Diffractometer, Scanning Electron Microscope/EDAX, Micro Hardness Tester, Pycnometer and Impedance Spectroscopy. The x-ray pattern at room temperature for deposited Ag/AgI/Ag does not show any phase transformation and the structure is dominated by γ -AgI, with the particle size is about 27.3 nm. There is a significant increase in ionic conductivity from 10^{-6} S/cm to 10^{-3} S/cm. The increase of the ionic conductivity is possibly due to the increasing number of Ag from 48.62% to 64.04% in the new composite Ag60'/AgI/Ag60' as confirmed by the result from EDAX. The microstructure measured by SEM shows an expansion of the matrix AgI after deposited by Ag. With increasing deposition time, the hardness increases, while the density decreases.

Key words : Composite-Electrolyte, AgI, Ionic conductivity, PVD

ABSTRAK

PENGEMBANGAN BAHAN BARU NANO KOMPOSIT ELEKTROLIT Ag/AgI/Ag DENGAN TEKNIK PVD. Bahan baru nanokomposit elektrolit Ag/AgI/Ag telah dibuat dengan teknik *Physical Vapour Deposition (PVD)*. Ag dideposisikan pada kedua sisi dari superkonduktor ionik AgI berbentuk koin dengan waktu deposisi 30 menit, 45 menit dan 60 menit. Beberapa karakterisasi pada hasil deposisi Ag/AgI/Ag seperti struktur kristal, struktur mikro, kekerasan, densitas dan konduktivitas ionik telah dilakukan dengan *Difraksi Sinar X, SEM/EDAX, Microhardness Tester*, Pycnometer dan Impedansi Spektroskopi. Pola difraksi sinar-x Ag/AgI/Ag pada suhu ruang tidak menunjukkan adanya transformasi fasa dan struktur kristal didominasi oleh fasa γ -AgI dengan ukuran partikel sekitar 27,3 nm. Ditunjukkan pula adanya kenaikan konduktivitas ionik dari 10^{-6} S/cm sampai dengan 10^{-3} S/cm. Kenaikan dari konduktivitas ionik disebabkan adanya kenaikan jumlah Ag di dalam komposit dari 48,62% menjadi 64,04% pada komposit baru Ag60'/AgI/Ag60' sebagaimana ditunjukkan dengan hasil pengamatan *EDAX*. Struktur mikro yang diukur dengan *SEM* menunjukkan adanya ekspansi dari matriks AgI setelah dideposisi oleh Ag. Dengan penambahan waktu deposisi, kekerasan meningkat sedangkan densitas menurun.

Kata kunci : Komposit elektrolit, AgI, konduktivitas ionik, PVD

INTRODUCTION

It is well known that solid electrolytes have many advantages over conventional liquid electrolytes. Recently, extensive studies have been carried out on solid electrochemical power sources that use various fast ionic conductors as solid electrolytes [1-4]. The most well known Ag⁺ ion conductor is based on the silver iodide, AgI. The crystalline AgI has three different phases α , β and γ . At room temperature, it is a mixture of β and γ -phases, but mostly dominated by a γ -AgI with the FCC structure and the ionic conductivity is low

$\sim 10^{-7}$ S/cm. However, β (Hexagonal) - phase transforms into the α -phase with the BCC structure at above the phase transition temperature ~ 147 °C, and the ionic conductivity increases up to $\sim 10^{-2}$ S/cm. For most electrical appliances such as battery and sensor work at ambient temperature, therefore it is important to find the material that has high ionic conductivity at least 10^{-3} S/cm (like α -AgI) at room temperature. In order to improve the ionic conductivity of AgI, several methods have been applied by many scientists, such as mixing

AgI with the second component as polymer, crystalline or glassy materials [5-8]. However, there is only a few works have been performed by depositing ions via sputtering or physical vapor deposition techniques [9-10]. The early work on depositing Ag via sputtering shows that the ionic conductivity of deposited AgI increases from 10^{-7} S/cm to 10^{-3} S/cm. In this case, thermal effect that occurred during sputtering has also changed partially the crystal structure from γ to β . In order to complete study of superionic AgI material, another deposition technique via Physical Vapor Deposition has been used. This work presents the effect of depositing Ag into AgI via a Physical Vapor Deposition technique. The deposition time varied at 30', 45' and 60' in order to obtain an optimum conductivity. Several characterizations such as, the electrical property, the hardness, the density, the crystalline phase and the microstructure of the new composite Ag/AgI/Ag will be described in this paper.

EXPERIMENTAL METHOD

Sample Preparation by PVD

The raw material used for this work is powder AgI (99.9%, Alfa Aesar) that has γ -phase. Several coin type electrolytes (pellets) were made using a Die from each 2 grams of the AgI powder at pressure 3000 Psi. The diameter (D), the thickness (l) and the weight (m) of the pellet were measured. Both sides of those pellet was then deposited by Ag target within 30', 45' and 60' via a Physical Vapour Deposition technique at K2I, P3IB-Batan. The system used is a Vacuum Coating unit TAAB. The new material obtained after depositing 30', 45' and 60' are composite materials and named Ag30'/AgI/Ag30', Ag45'/AgI/Ag45' and Ag60'/AgI/Ag60', respectively.

Sample Characterization

To observe the microstructure of the new composite we performed the Scanning Electron Microscope measurement. The atomic fraction in new composite was observed by using EDAX. Both instruments used are SEM 515 Philip dan EDAX PV 9900 Philip at Industrial Material Division, PTBIN-BATAN. The hardness and density of the new composite were measured respectively by Micro Hardness Tester, Shimadzu type-M at BKI, PTBIN-BATAN and by using a Pycnometer at Advanced Materials Division, PTBIN-BATAN. The crystalline phase of the new composites Ag/AgI/Ag were measured by using an X-ray diffractometer Shimadzu XD-610 at Industrial Material Division, PTBIN-BATAN. The ionic conductivity of the new composites was measured by an LCR Hi Tester Hioki 3522-50 at Advanced Materials Division, PTBIN-BATAN.

RESULTS AND DISCUSSIONS

Microstructure, Density and Hardness

After depositing Ag into AgI, visually the color of the pellet surface has changed from yellow to silver. The microstructures of AgI, Ag30'/AgI/Ag30', Ag45'/AgI/Ag45' and Ag60'/AgI/Ag60' obtained via SEM (enlargement 5000x) are shown in Figures 1a, 1b, 1c and 1d, respectively, and their atomic fraction from EDAX are listed in Table 1. The results suggested that some Ag ions from the target occupy the hole in the AgI matrix, so that atomic fraction of Ag increases from 52.7 to 67.7 %, while the atomic fraction from I decreases (Table 1). The deposition of Ag after certain time may cause the Ag-I link becomes looser, and some Ag ions may move from its original positions and may be substituted by the new deposited Ag ions. The extra silver ions may diffuse from one to another, making new link of conduction pathway, thus increasing the conductivity.

The results show that after depositing Ag within 30 and 45 minutes, the density decreases from 5.48 to 5.41 g/cm³, but it increases again to 5.48 g/cm³ within

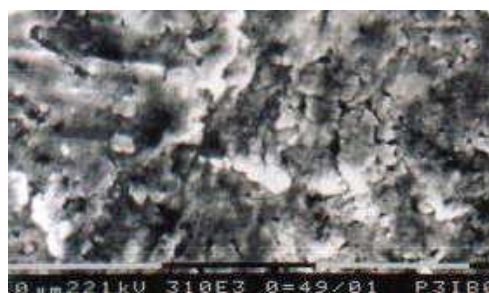


Figure 1a. Microstructure (SEM) of AgI before deposition.

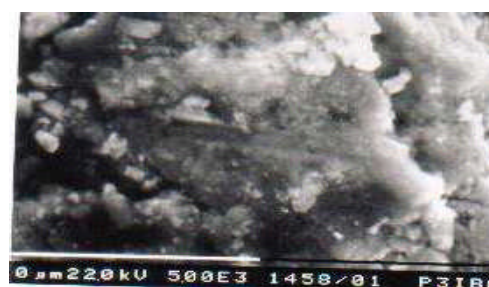


Figure 1b. Microstructure (SEM) of Ag30'/AgI/Ag30'

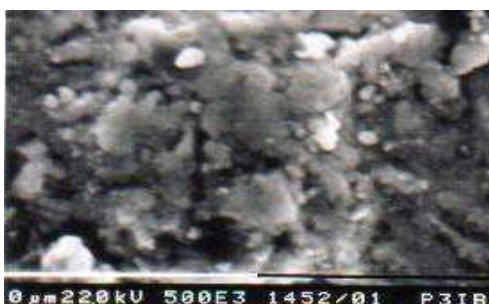


Figure 1c. Microstructure (SEM) of Ag45'/AgI/Ag45'



Figure 1d. Microstructure (SEM) of Ag60'/AgI/Ag60'

60 minutes. It seems, that at the beginning the loose of Ag-I link reduces the density of the matrix AgI but not enough Ag ions to occupy the all vacancies, however with further depositing time, number of Ag ions have filled the vacancies, so that both the density and hardness increase (see Table 1).

Table 1. Density, Hardness and atomic fraction of Ag/AgI/Ag with different deposition times.

Sample	Density (ρ) (gr/cm ³)	Hardness (HV)	Atomic %		Weight %	
			Ag	I	Ag	I
Ag0'/AgI/Ag0'	5.502	12.96	52.68	47.32	48.62	51.38
Ag30'/AgI/Ag30'	5.480	8.968	62.54	37.46	58.66	41.40
Ag45'/AgI/Ag45'	5.407	10.42	62.88	37.15	58.99	41.01
Ag60'/AgI/Ag60'	5.476	11.21	67.68	32.32	64.04	35.96

Note : HV : Vickers Hardness number

Crystal Structure

The x-ray diffraction patterns of the AgI and Ag/AgI/Ag with deposition time 30, 45 and 60 minutes are shown in figures 2a, 2b, 2c and 2d, respectively. The Rietveld Analysis has been used to analyse the X-ray diffraction patterns for new composite samples. Figure 2a shows the strong Bragg peak at 2θ = 23.5° that

corresponds to the γ-AgI phase [11] dominates the structure, while the β-phase was not detected. After 30 minutes deposition, the Bragg peak of γ-AgI at 2θ = 23.5° still dominates the structure, but a new peak corresponds to the Ag appears at 2θ = 37.9°. The weight fraction of γ-AgI:Ag is 0.86:0.14 showing that during 30 minutes depositing time, 14.4% of Ag mixed with AgI in the new composite Ag30'/AgI/Ag30'. After 45 minutes, the AgI structure of Ag45'/AgI/Ag45' does not change but the intensity of γ-AgI at 23.5° decreases, with the new fraction 73 %. Meanwhile, the intensity of peak of Ag at 37.9° increases and the weight fraction increases to 27%.

Further increasing deposition time, the composite Ag60'/AgI/Ag60' has been saturated, no more free Ag ions can fill the vacancies, but some of them are probably linked with the I and stabilized the existing γ-AgI and possibly β-AgI. It is shown by the increasing of the intensity at 23.5° from the mixture of γ-AgI and β-AgI. The weight fraction increases up to 90% while the Ag decreases to 10 %.

The particle size can be derived from the full width of half maximum (FWHM) of the Bragg peaks in the X-ray pattern using equation (1).

$$t = 0.9 \lambda / B \cos \theta \dots\dots\dots (1)$$

where λ, B and θ are the wavelength used in the x-ray target (1.54 Å), the width (fwhm) and the scattering angle, respectively. The grain size of γ-AgI is about 27.4 nm, before and after depositions, while the size of depositing Ag is 6.8 nm. The results show that the existence of depositing Ag via PVD, does not change structurally AgI, either the phase or the particle size of γ-AgI. We assume that besides the size of Ag which is too small to destruct the structure, no thermal effect occurs during deposition, in contrast to

Table 2. FWHM and weight fraction of Ag/AgI/Ag with different deposition times (Refinement results).

	2θ	AgI		Ag30'/AgI/Ag30'		Ag45'/AgI/Ag45'		Ag60'/AgI/Ag60'	
		FWHM	W %	FWHM	W %	FWHM	W %	FWHM	W %
γ-AgI	23.5	0.20	0.9	0.23	0.86	0.28	0.73	0.17	0.90
Ag	37.9	0	0.1	0.34	0.14	406	0.348	0.32	0.10

Note: W % = weight percent

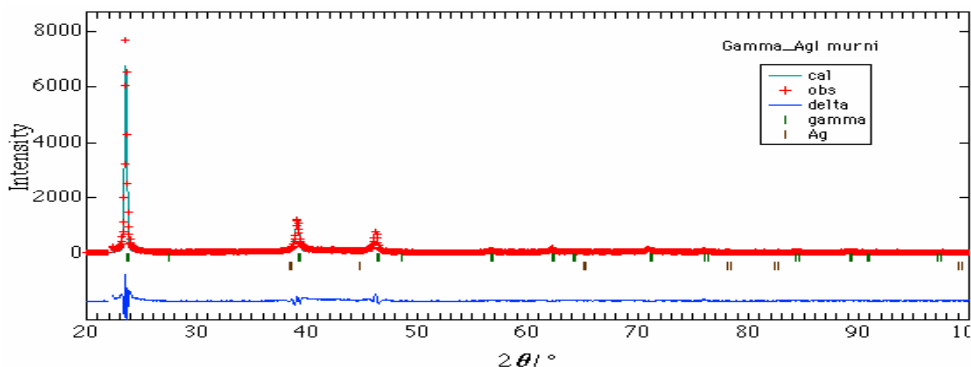


Figure 2a. X-ray diffraction pattern and refinement result on AgI

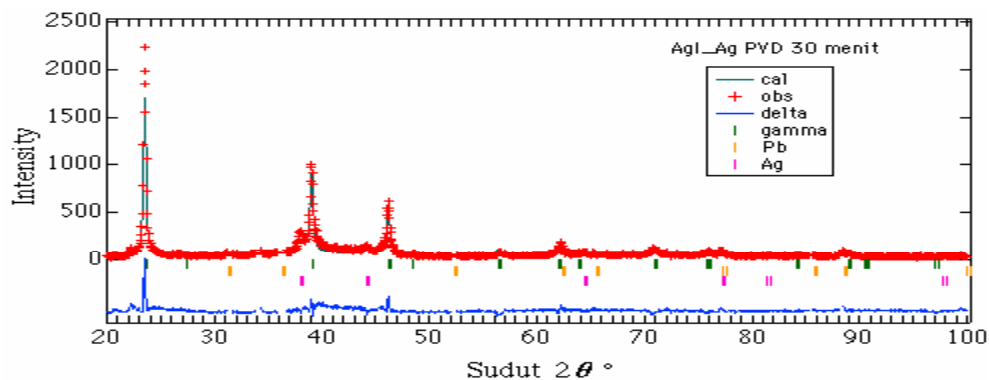


Figure 2b. X-ray diffraction pattern and refinement result on Ag30'/AgI/Ag30'

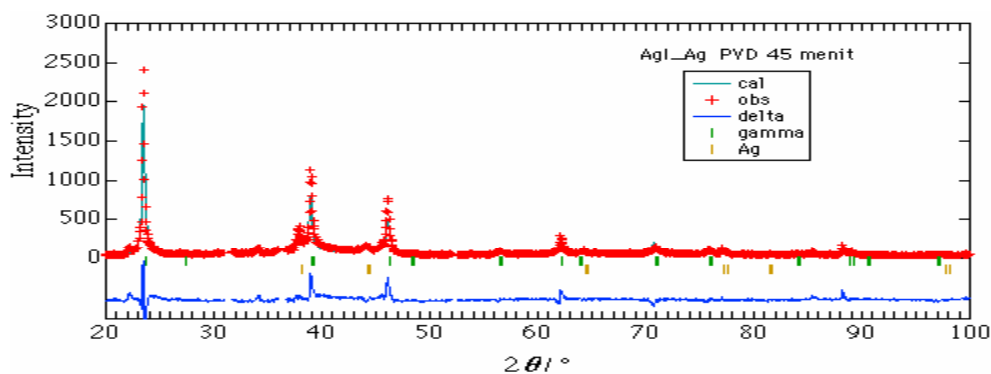


Figure 2c. X-ray diffraction pattern and refinement result on Ag45'/AgI/Ag45'

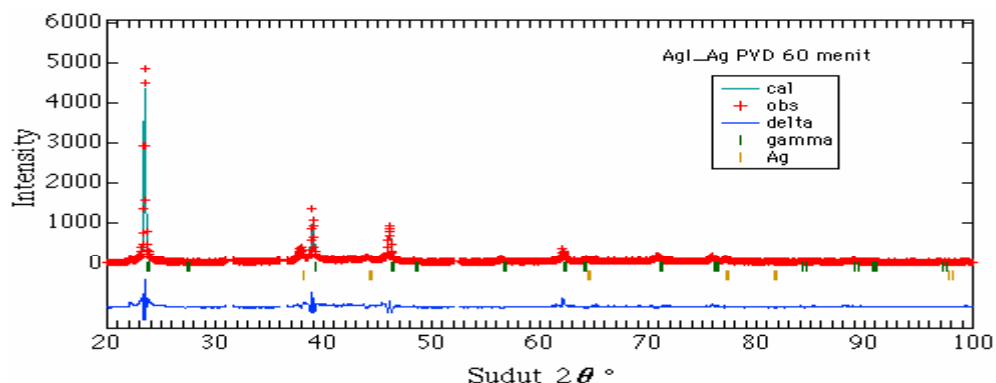


Figure 2d. X-ray diffraction pattern and refinement result on Ag60'/AgI/Ag60'

the results obtained via sputtering technique which shows the phase transformation of γ -AgI to β -AgI [9-10].

Ionic Conductivity

The frequency dependent of the conductivity on new composites Ag/AgI/Ag with various deposition times have been measured at room temperature by using an LCR meter. The frequency range covered by the measurement is from 0.1Hz to 100 kHz at constant voltage 1 volt. Figure 3 shows the logarithmic of conductivity as a function of logarithmic of frequency for AgI, Ag/AgI/Ag with deposition times 30', 45' and 60'. It is shown that the ionic conductivity increases with deposition time up to 45'

with the values from $\sim 10^{-6}$ S/cm to $\sim 10^{-3}$ S/cm, then it decreases again with deposition time 60'. The result shows that the optimum value of the conductivity has been achieved for the deposition time 45', and this is possibly due to the occupancy of the Ag ions in the matrix AgI has been optimized and reached saturation, further addition of Ag ions will even decrease the mobility of Ag ions thus decreasing the ionic conductivity. This phenomena is also found for other physical properties such as density and hardness. The result is confirmed also by decreasing the weight fraction of Ag compared with the γ -AgI on the X-ray diffraction result.

The frequency dependent of conductivity is explained in the model known as a *Universal frequency Response* developed by *Jonscher et al* [12] via relation

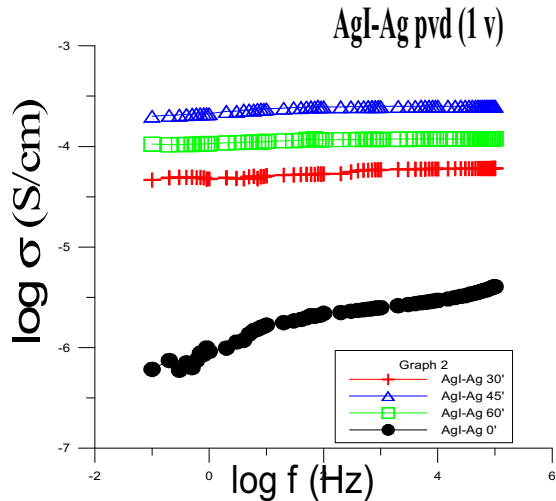


Figure 3. Frequency dependent of the Ionic conductivity on AgI and Ag/AgI/Ag with deposition times 30', 45' and 60'.

$$[\sigma] \gg f^s \dots\dots\dots (2)$$

where σ and s are conductivity and *exponent power*, $0 < s < 1$. The value of s has a limit value 1 and depends on the temperature. It can be described in the equation

$$\sigma = \sigma_0 f^s \dots\dots\dots (3)$$

In order to analyse the frequency dependent of the ionic conductivity in more detail, the data in Figure 3 was divided into two different frequency ranges due to their different physical meaning. The low frequency range started from 0.1 Hz up to 1 Hz, represents an *ionic hopping* while medium frequency range from 1 Hz to 100 kHz represent the vibrational motions. In the medium range the curve shows a plateau meaning that conductivity is independent with the frequency. Sometimes this area can be related to the DC conductivity. The two frequency regimes were then fitted by using equation :

$$\log \sigma \gg \log \sigma_0 + s \log f \dots\dots\dots (4)$$

where $\log \sigma_0$ is the conductivity at frequency 1 Hz and s exponent power. Table 3 shows the parameters obtained from the fitting. The value of conductivity at 1 Hz and 1 volt for AgI, Ag30'/AgI/Ag30', Ag45'/AgI/Ag45', and Ag60'/AgI/Ag60' are respectively 1.03×10^{-6} S/cm, 1.5×10^{-5} S/cm, 1.03×10^{-3} S/cm, and 1.1×10^{-4} S/cm.

The results show that the ionic conductivity of new composites Ag/AgI/Ag increases by a factor 100-1000 times compared with the conductivity of original AgI. The maximum conductivity $\sim 1.03 \times 10^{-3}$ S/cm is achieved for deposition time 45' while the original AgI has the ionic conductivity of about $\sim 10^{-6}$ S/cm. It can be concluded here, that the new composite electrolyte with better ionic conductivity at room temperature has been obtained via PVD technique.

Table 4. The exponent power parameters and DC conductivity for composites Ag/AgI/Ag with different deposition time.

Sample	Fitting 1		Fitting 2	
	Log f (-1)Hz – log f 2Hz		Log f 2Hz – log f 5 Hz	
	S ₁	Log σ_{01}	S ₂	Log σ_{02}
Ag0'/AgI/Ag0'	0.205	-6.03	0.099	-5.87
Ag30'/AgI/Ag30'	0.016	-4.31	0.012	-4.27
Ag45'/AgI/Ag45'	0.034	-3.66	0.002	-3.61
Ag60'/AgI/Ag60'	0.019	-3.96	0.002	-3.93

CONCLUSION

The new composites Ag/AgI/Ag with different deposition times 30', 45' and 60' have been developed via PVD technique. The microstructure obtained by SEM shows that the vacancy of AgI matrix increases during the deposition time, and but some of them are occupied by new deposited Ag-ions. The exchange of Ag ions from or to AgI matrix cause the mobility of charge carriers increases and diffuses leading to increase in ionic conductivity from 10^{-6} S/cm to 10^{-3} S/cm. The atomic fraction of Ag in the sample increases from 57 % to 67.68 %, while the fraction of I atom decreases.

However, the optimum deposition time occurs at 45 minutes, meaning that the amount of Ag to be deposited has reached the optimum value and further increasing amount of Ag will saturate and decrease the ionic conductivity. The crystal structure of new composite consists of γ -AgI and Ag. The maximum weight fraction of Ag is achieved at deposition time 45'. Interestingly, the results show that the grain size of the new composite is in the nano size γ -AgI and Ag are ~ 270 and 68 \AA , respectively, therefore this new composite, is also called as a nano composite superionic. The development of new composite electrolyte with nano crystalline size will give more opportunity to the application of the new solid state battery and sensor in the near future.

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