Int. J. Electrochem. Sci., 7 **(2012)** 2448 - 2454

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Effect of Zn-Substitution on the Mechanical, Thermal and Conductivity of AgI rich AgI–ZnI_2 Solid Solutions

Ng Meng Nee, Mohd Rafie Johan[*]

Nanomaterials Engineering Research Group, Advanced Materials Research Laboratory, Department of Mechanical Engineering, University of Malaya, Lembah Pantai 50603, Kuala Lumpur, Malaysia
[*]E-mail: mrafiej@um.edu.my

Received: 19 November 2011 / *Accepted:* 2 February 2012 / *Published:* 1 March 2012

The composition of silver iodide rich solid solutions (x)AgI – (1-x)ZnI_2 ($0.5 \leq x \leq 1$) were prepared using mechano-chemical technique. Addition of ZnI_2 content reduces the degree of crystallinity of samples. Sample with 70% AgI shows the most amorphous structure. From the DSC curve, the glass transition temperature (T_g) of 70% AgI is 80.91ºC. The increasing ZnI_2 content decreases the T_g of AgI-ZnI_2 system. 70% of AgI exhibited the highest conductivity at room temperature, which is 1.913×10^{-4}S/cm. The flexural modulus and ultimate flexural strength for 70% AgI are 0.069MPa and 0.058MPa respectively. Sample with 70% of AgI was used for battery fabrication. Open circuit voltage and the internal resistance obtained are 0.654V and 4.4Ω respectively.

Keywords: Silver iodide; Zinc iodide; Ionic conductivity; Open circuit voltage; Internal resistance

1. INTRODUCTION

Silver ion conducting solid electrolytes have attracted widespread interest due to their possible applications in solid state electrochemical devices [1-2]. The majority of these solids have been prepared with silver iodide (AgI) as the host compound. AgI is well known materials as an ionic conductor (Ag^+) at ambient temperature. It undergoes a first order structural phase transition (wurtzite (β)/ zincblende (γ)/ body centered cubic (α) phase) at 147°C to a highly dynamic superionic state, with an extremely high ionic conductivity ($\sigma \sim 0.1 - 1.0 \Omega cm^{-1}$) comparable to those of liquid state while still showing long range crystalline order (bcc structure) [3]. AgI exhibits other interesting behavior such as a highly disordered cation distribution, an essentially rigid crystal framework provided by the anion sublatice and low activation energies for cation diffusion and conduction. Study of the effects of

chemical substitution on AgI provides further insight into the complexities of the phase transition thus helps arriving at a mechanism governing the ion transport within the crystal lattice [4]. Chemical substitution has been used extensively to modify either the magnitude of ionic conductivity or the transition temperature separating superionic and covalent phases in various solid electrolytes. In the present investigation, we seek to determine the effect of zinc substitution on the ionic conductivity, mechanical properties and phase transition behavior of (x)AgI-(1-x)ZnI_2 ($0 \leq x \leq 1$) system. As far as AgI is concerned, addition is zinc, the performance of solid state batteries with zinc as cathode active material is also described.

2. EXPERIMENTAL

AgI was prepared by the chemical reaction of silver nitrate ($AgNO_3$) and potassium iodide (KI) as starting material. They were weighted and dissolved in 1000 ml of distilled water to produce the co-precipitation of AgI. The AgI was then washed with distilled water and dried in oven at 50ºC for 1 day. The AgI was then mixed with ZnI_2 powder thoroughly using ball mill at different composition. The mixed powder was pressed at 25 tons to form pellets. Structural characterization was performed using a Siemen D500 X-ray diffractometer. The ionic conductivity was measured using Hioki 3531 Z Hi-Tester impedance spectroscopy in the frequency range of 50Hz to 1MHz. The thermograms of the samples were obtained using Metler DSC 820 at a heating rate of 10°Cmin^{-1}. The mechanical properties were measured using three point bending flexural test.

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction (DSC) Analysis

Fig. 1 shows the powder XRD patterns of the as-prepared samples.

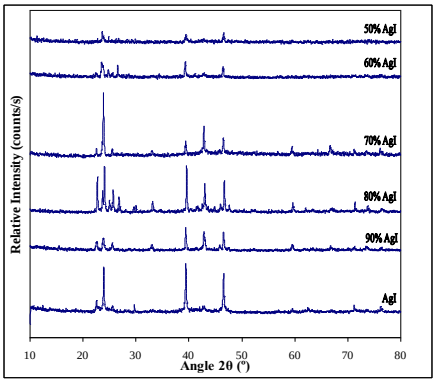

Figure 1. XRD pattern for silver rich AgI-ZnI_2 system at various compositions

The patterns consist of three prominent Bragg peaks at 24 º, 39 º and 47 º which indicate the crystalline nature of AgI. As ZnI_2 was added into AgI, there are new peaks appear at angle of 22 º, 26 º, 33 º and 43 º which varies greatly from the pure AgI.

Table 1. Compositions of AgI-ZnI_2 system with electrical conductivity, ultimate flexural strength and flexural modulus

Sample	Composition	σ (Scm^{-1})	Ultimate Flexural Strength (MPa)	Flexural Modulus (MPa)
1	AgI	4.970×10^{-6}	0.036	0.105
2	0.9 AgI-0.1 ZnI_2	1.525×10^{-4}	0.036	0.061
3	0.8 AgI-0.2 ZnI_2	1.318×10^{-4}	0.047	0.045
4	0.7 AgI-0.3 ZnI_2	1.913×10^{-4}	0.058	0.069
5	0.6 AgI-0.4 ZnI_2	4.010×10^{-5}	0.040	0.079
6	0.5 AgI-0.5 ZnI_2	1.331×10^{-4}	0.054	0.098

3.2 Differential Scanning Calorimeter (DSC) Analysis

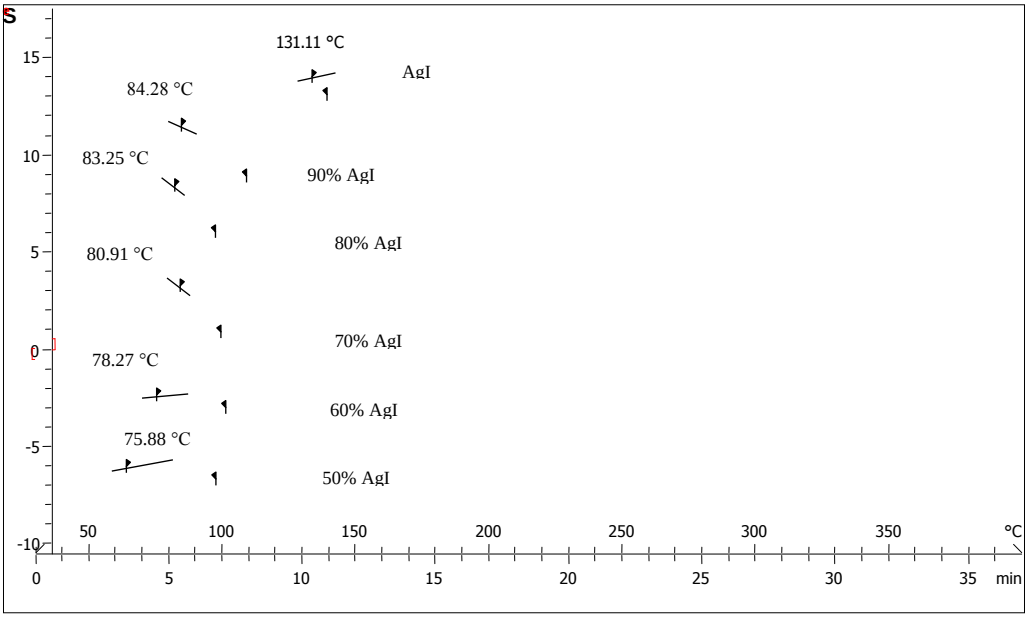

Figure 2. DSC curve for silver rich AgI-ZnI_2 system at various compositions

The variation intensities of the peaks for different compound were observed. The amorphous hump observed indicated the increased of amorphous character in the compound. These suggest that part of AgI was remained salt-free while other was salt-contained. As a result, it transformed into the amorphous phase and hence displays less crystallinity [5]. XRD pattern at various compositions shows

the disappearance and nucleation of new peaks with the addition of ZnI_2. These indicate of the complexation of AgI and ZnI_2. The added ZnI_2 distrupted the crystalline structure of AgI and converts it into a more amorphous phase. Thus, it reduces the degree of crystallinity with randomly distributed stacking faults [6].

Fig. 2 shows a decrease of glass transition temperature, T_p with the increases of ZnI_2 content. The sample becoming unstable and lead to the phase transition. The pure AgI undergo phase transformation at the temperature of 131ºC with the addition of ZnI_2. This was well explained by the presence of amorphous phase in the XRD results due to the increasing of ZnI_2 content [8].

3.3 Electrical Conductivity Analysis

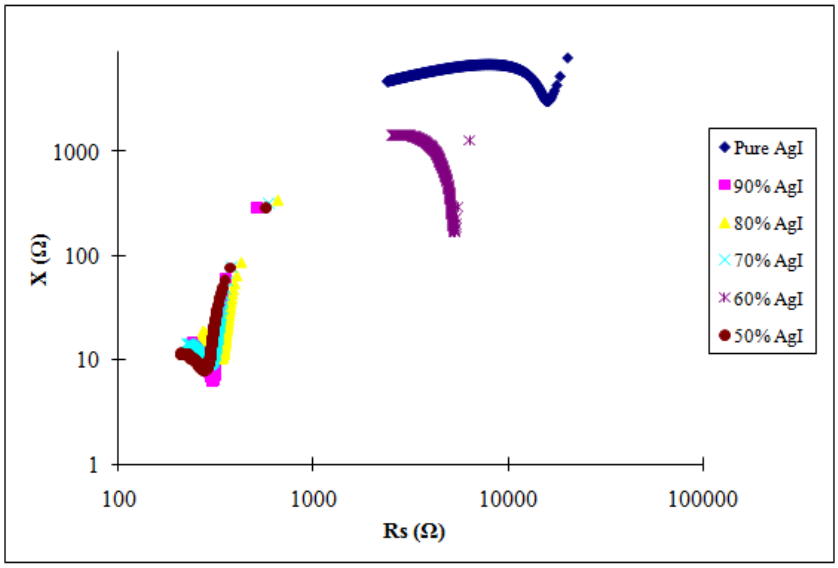

Figure 3. The cole-cole plot for silver rich AgI-ZnI_2 system at various compositions

From Table 1 the conductivity varies randomly with the increasing of ZnI_2 content. This is due to the change of ionic mobility in the presence of Zn ions in the host material. Composition with 70% wt of AgI exhibits the highest conductivity that is 1.913×10^{-4} S/cm while the pure AgI is the lowest. It shows that the addition of ZnI_2 content contributed to the enhancement of ionic conductivity by increasing the number of charge carrier and ionic mobility. Furthermore, it is the most amorphous sample, which has a lower degree of crystallinity [8]. The co-existence of different bonding, Ag-I and Zn-I, is essential to originate the superionic behavior as suggested in some models. Fig. 3 shows typical impedance plots obtained for all compositions. A capacitive arc at high frequencies is observed, which is associated with the kinetics of the change transport in the bulk of the sample. A linear region is observed adjacent to this arc at low frequencies that is attributed to the change transfer at the

electrode/sample interface. Table 2 shows the temperature dependence of the ionic conductivity for the sample with the composition $0.7AgI\text{-}0.3ZnI_2$.

Table 2. Temperature dependent of conductivity for sample with 0.7 AgI-0.3 ZnI_2

Sample	Temperature (ºC)	Conductivity (S/cm)
1	25	1.913×10^{-4}
2	50	6.985×10^{-4}
3	70	1.060×10^{-3}
4	90	1.190×10^{-5}
5	110	4.902×10^{-6}
6	130	1.285×10^{-6}

Table 2 shows that the ionic conductivity increases from 25ºC to 70ºC and decreases at 90ºC. As the temperature increases, the silver salts get dissociated which resulted in increases of Ag^+ concentration. The decreases of conductivity are due to the short range ordered clusters embedded in a highly conductive disordered medium. As the temperature was further increased, formation of clusters will blocked the pathways for ions migration. As a results the mobility of ion will be decreased [7-8].

3.4 Flexural Analysis

From Table 1, sample with 70% of AgI exhibit the highest ultimate flexural strength, which is 0.058MPa while both pure and 90% of AgI have the smallest one, which is 0.036MPa. Besides, pure AgI shows the highest flexural modulus which is 0.105MPa while 80% of AgI exhibit the lowest flexural modulus which is 0.045MPa. There is a correlation between high conductivity and high mechanical properties which occurred at 70% AgI.

3.5 Open Circuit Voltage (OCV)

The OCV for the cell fabricated from the $0.7AgI\text{-}0.3ZnI_2$ electrolyte using zinc as the active material is 0.654V. This is very close to the thermodynamic value related to the AgI formation that is 0.690V at room temperature [9].

3.6 Internal Resistance

Fig. 4 shows the voltage-current character of $0.7AgI\text{-}0.3ZnI_2$. Hence, the internal resistance of sample is 4.4Ω. The lower the internal resistance, the less restriction the battery encounters in delivering the needed power spikes. A high mW reading can trigger an early 'low battery' indication on

a seemingly good battery because the available energy cannot be delivered in the required manner and remains in the battery. Interaction of iodine with the Ag^+ ions at room temperature may lead to the formation of β phase AgI. This β phase AgI can increase the cell's internal resistance [10].

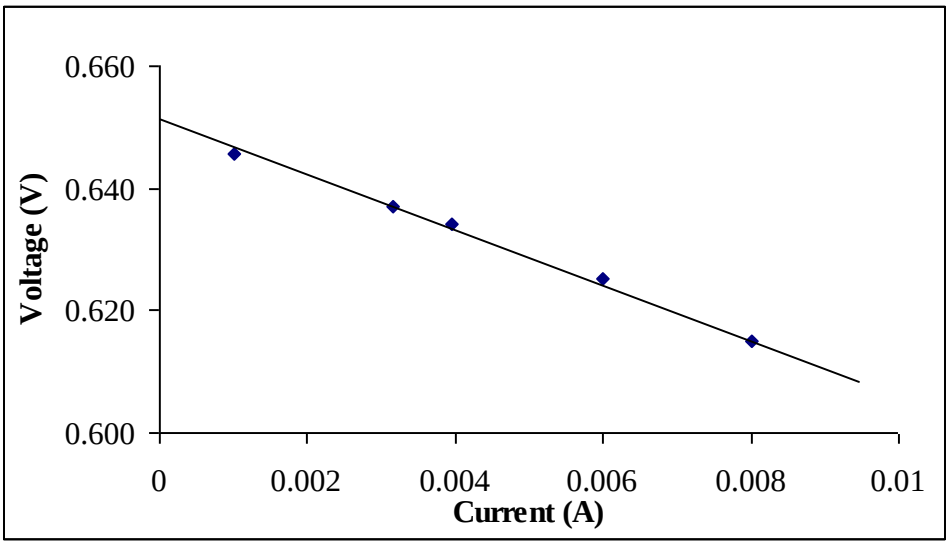

Figure 4. Voltage-current characteristics of $0.7AgI\text{-}0.3ZnI_2$ battery

4. CONCLUSION

The ionic conductivity of the sample is related to the crystalline structure where the most amorphous sample (70% AgI) shows the highest conductivity of 1.913×10^{-4}S/cm. The addition of ZnI_2 content into AgI has improves the ionic conductivity significantly. The effect of phase transition and degree of cystallinity are investigated by XRD and DSC analysis. The most amorphous phase occurs at 70% AgI and the T_g obtained is 80.91ºC. 70% AgI shows the highest ultimate flexural strength, which is 0.058MPa. The temperature dependence conductivity was performed at sample 70% AgI, the result show that conductivity rises from room temperature to 70ºC and decrease from 90ºC to 130ºC. Battery was fabricated using 70% AgI. The open circuit voltage and internal resistance were determined, which is 0.654V and 4.4Ω, respectively.

References

1. B. V. R. Chowdari, Q. G. Liu and L. Q. Chen, *World Scientific* (1990).
2. B. V. R. Chowdari, S. Chandra, S. Singh and P. C. Srirastava, *World Scientific*, (1990).
3. S. Chandra, *Superionic Solids*, (1981).
4. K. Shahi, *Phys. Status Solid*; A 41 (1977) 11.

5. M. H. Nordin, Z. A. Rahman, M. R. Johan, S. Anandan, and A. K. Arof, *IFMBE Proceedings* 15, (2007) 144.
6. P. S. Kumar, P. Balayab, P. S. Goyalb and C. S. Sunandana, *Journal of Physics and chemistry of Solids* 64, (2002) 961.
7. H. K. Farizul, S. A. Aishah, D. Suhardy, A. S. Saiful and M. N. Salleh, Proceedings of the 1st International Conference on Natural Resources Engineering & Technology. (2006) 262-273.
8. R. C. Agrawal, M. L. Verma, R. K. Gupta, R. Kumar and R. M. Chandola, *Journal of Ionics* 8 (2002) 426.
9. B. Scrosati and G. Pistoia, *Journal of Applied Electrochemistry* 4 (1974) 201.
10. A.K. Arof, Thesis, University of Malaya, Kuala Lumpur (2006).