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Mott-Schottky Analysis of Laboratory Prepared Ag_2S-AgI Membrane Electrode

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Abstract

Mott-Schottky analysis has been carried out to study the semiconducting behavior of Ag_2S-AgI material, which is used as membrane material in iodide ion sensors. Polycrystalline Ag_2S-AgI materials with mixing ratios 1:1 was prepared by co-precipitation method and Mott-Schottky analysis was carried out. The impedance was recorded using a Solartron 1280 Schlumberger frequency response analyzer at 5 KHz and 10 mV perturbing signal. A straight line with a positive slope is observed between + 0.2 V to – 0.2 V (SSE) indicating n-type semiconductor behavior of polycrystalline Ag_2S-AgI membrane. The donor concentration N_D was calculated from the slope using dielectric constant of Ag_2S-AgI. The values obtained are ~ 6 orders of magnitude lower than in metals. This is an important implication for the charge and potential distribution at the semiconductor/electrolyte interface. The Mott Schottky analysis has shown that the present materials are n-type semiconductors with donor defect concentration of $7.4x10^{17}/cm^3$.

Keywords : *Ag_2S-AgI electrode, Mott-Schottky Analysis*

Introduction

Silver sulphide-silver iodide (Ag_2S-AgI) material was initially used by Pungor in 1961 for electrode preparation[1]. Since then, it was studied and characterized by different authors[2-4] in order to find its application in different analytical fields[5-6]. The electrochemical characterization is one of the important parameter to study the mechanistic study of ion selective electrode. Very few literatures regarding the study on electrochemical characterization of Ag_2S-AgI electrode are found. Recently, their electrochemical property was studied in our previous work[7]. In this study, semiconducting properties have been discussed using results from electrochemical impedance studies. In semiconductor electrochemistry, the space charge region at the electrode/electrolyte interface is fundamental importance. Space charge capacitance behavior can be studied by electrochemical impedance spectroscopy (EIS). EIS provides valuable information on the electron-transfer resistance and capacitive behavior of electrode-electrolyte interface.

It is generally assumed that Frankel defects are majority. There is a metal deficiency in crystal lattice so migration of silver ions was proposed. Experiments on semiconductor electrolyte contacts are an interesting alternative to obtain information on semiconductor properties of semiconductor, the type of semiconductivity and the acceptor or donor density[8]. The interface between a solid ionic conductor (AgBr) and a liquid electrolyte was first discussed by Grimely and Mott[9]. Buck et al[10] studied experimentally the electrical properties of AgCl single crystals in contact with an electrolytic solution. The main experimental problem is the high electrode resistance at room temperature.

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In the present study, we will report on the electrochemical properties of Ag_2S-AgI membrane electrode in aqueous electrolytic solutions. The electrode of composition 1:1, mole ratio of Ag_2S-AgI was fabricated in the laboratory and characterized by electrochemical techniques. Then capacitance measurements were done to evaluate the donor defect concentration of the materials by Mott Schottky analysis. Using capacitance values carrier concentrations (donor density) can be calculated by following Mott-Schottky equation (1). According to the Mott-Schottky equation, the inverse square of space charge capacitance C_{sc} depend linearly with the potential applied as follows.

$$1/C_{sc}^2 = 2\,(E-E_{fb}) / (\varepsilon\, \varepsilon_o e_o\, N_D) \qquad (1)$$

Where,

C_{sc} = space charge capacitance
E = applied potential
E_{fb} = flat band potential
N_D = donor density of electrode material
ε_o = dielectric permittivity
ε = relative dielectric constant
e_o = elementary charge

Experimental

Ag_2S-AgI powder was prepared in laboratory and was pressed into pellets at room temperature under a pressure of 10 tons using KBr pellet making machine. The pellets were contacted with a copper wire using silver disk and silver paint for good ohmic contact. The electrode was tightly sealed with epoxy resin and the surface was carefully polished with 2000 grit size sand paper. The electrode is characterized in terms of its response behavior, response time. The details were given in our previous study[7].

Capacitance measurement was performed using a Solartron 1280 Schlumberger frequency response analyzer. The impedance spectra were recorded 5 KHz and 10 mV perturbing signals at scan rate of at 5 mV/s in 10^{-1} M KNO_3, potential was swept from -0.2 V to + 0.2 V and Z-view software (version 2.6 b) was used for evaluating the impedance spectra.

Results and Discussion

Measurement of impedance

The experiments were carried out in the frequency range of 5 kHz to 10 mHz at open circuit potential using 10^{-1} M KNO_3 and in varying the iodide ion concentration of 10^{-3} M KI and 10^{-2} M KI. EIS data were analyzed in terms of equivalent circuit model in order to match the measured data.

Figure 1 shows the model of present electrode with 3 distinct zones- 1st zone represents the silver back contact/membrane interface, 2nd zone represents the bulk membrane, 3rd corresponds to membrane/electrolyte interface. In 1st zone, there is a possibility of electron transfer between silver disk and bulk membrane. In 2nd zone, both ionic and electron transfer processes are possible as there is Frankel type of lattice defect in bulk membrane where silver ions can migrate from one interstitial site to other interstitial site or in defect sites or push and replace other silver ions while in 3rd zone, charge transfer as well as ionic transfer processes are possible.

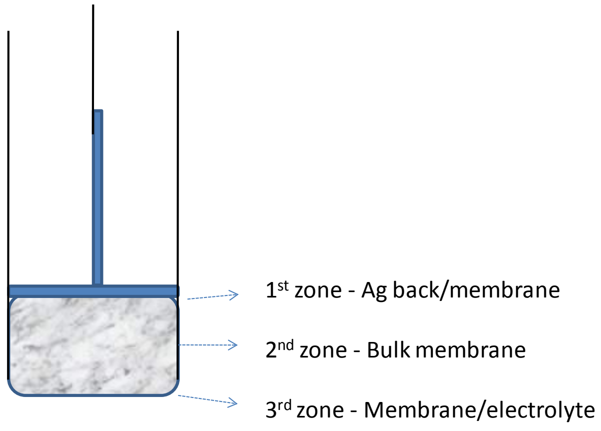

Figure 1: *Electrode model showing 3 different zones; (1) Ag-back contact/membrane, (2) bulk membrane, and (3) membrane/electrolyte interface.*

The EIS results obtained by electrode in 3 different electrolytes 10^{-1}M KNO_3, 10^{-3}M KI and 10^{-2}M KI were expressed in Nyquist plots shown in **Fig 2 a-c** respectively. The points are experimental data. Nyquist plot showed a significant change in impedance response in higher concentration of iodide showing 2 time constants, one at higher frequency region and second one at lower frequency region.

Fjeldy et al.[11], Bralic et al.[12] have observed 2 time constants in LaF_3 membrane electrode having solid state contact. Fjeldy and Bralic proposed time constant at high frequency is due to bulk properties of the membrane[13] with bulk resistance and capacitance which are independent on experimental condition. In this study, time constant at high frequency region is not distinct but in higher iodide concentration it is observed in depressed semi circle form and is assumed for silver back contact as in Bralic et al[14] and Martinhon et al[15]. The time constant at lower frequency region was prominent in all electrolytes and fitted with the Warburg diffusion and an RC circuit component. It was found that a good fitting could be only observed by using RC circuit (charge transfer resistance in parallel with a double layer capacitance) as suggested by Fjeldy[11] and Bralic[12]. Therefore, in this study, time constant at lower frequency region was assigned to charge transfer resistance and double layer capacitance at the membrane/electrolyte interface.

The equivalent circuit of present electrode can be figured by $R_{sol} + [R_{ct}/C_{dl}]_1 + [R_{ct}/C_{dl}]_2$**.** Where, R_{sol} corresponds to solution resistance, $[R_{ct}+C_{dl}]_1$ corresponds to charge transfer resistance and double layer capacitance of Ag/Ag_2S-AgI back contact and $[R_{ct}/C_{dl}]_2$ corresponds to charge transfer resistance and double layer capacitance of membrane Ag_2S-AgI/solution interface. Fitting were done by using Z fit software tools [version 2.6 b].The lines in **Fig 2a-c** show the fitted results by using equivalent circuit**.** It is obvious that a good fitting was obtained in all frequency range.
From the fitted data, the double layer capacitance were obtained, which are given in **Table 1.**

Table 1*: Capacitance obtained from the impedance spectra recorded for 1:1 electrode in 10^{-1}M KNO_3, 10^{-3} M KI, and 10^{-2}M KI solution.*

Ag_2S:AgI	10^{-1} M KNO_3	10^{-3} M KI	10^{-2} M KI
	C/µF	C/µF	C/µF
1:1	8.9 x 10^{-5}	2.1 x 10^{-4}	3.1 x 10^{-4}

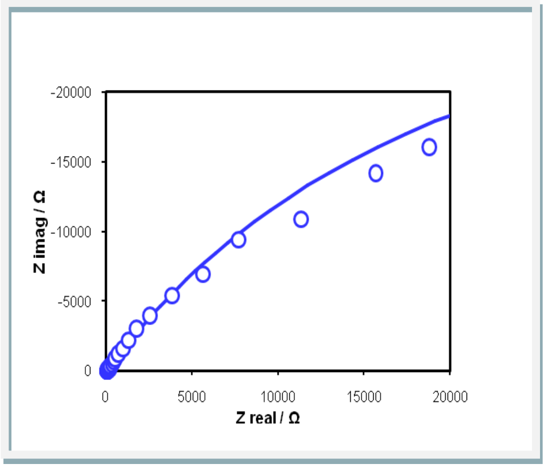

Fig 2-a: *Nyquist plot of impedance response obtained on ion selective electrode in 10^{-1} M KNO_3 at open circuit potential.*

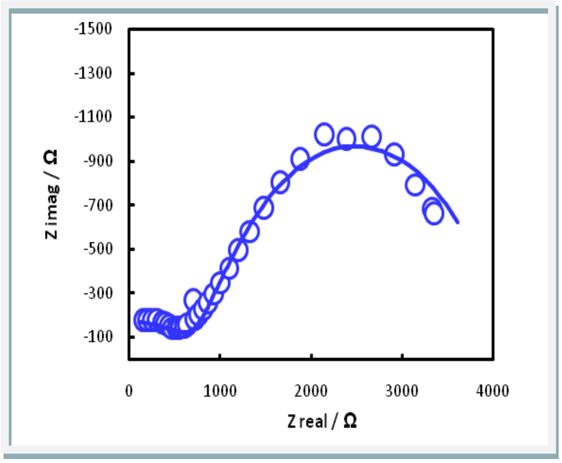

Fig 2-b: *Nyquist plot of impedance response obtained on ion selective electrode in 10^{-3} M KI at open circuit potential.*

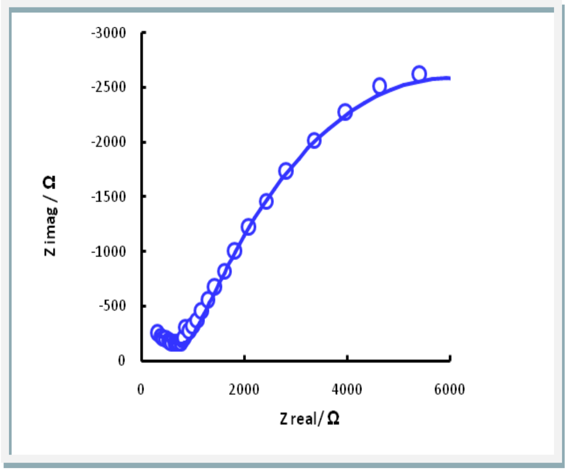

Fig 2-c : *Nyquist plot of impedance response obtained on ion selective electrode in 10^{-2} M KNO_3 at open circuit potential.*

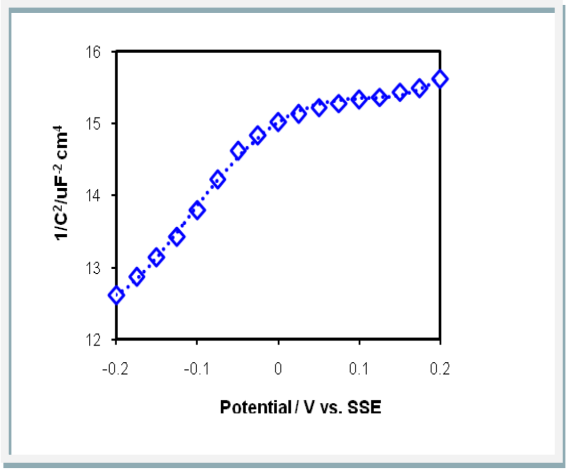

Fig 3 : *Mott-Schottky plot of 1:1electrode in 10^{-1}M KNO_3*

Measurement of donor defect concentration

When Ag_2S-AgI electrode is polarized with respect to the solution by means of an external emf source, the membrane/electrolyte interface constitutes an electrical double layer with a negative charge located at the solution side and the corresponding positive charge at the membrane side. This positive charge will diffuse because of the relatively small charge carrier concentration in the membrane and a sub-surface or depletion layer is developed. As a result, an interfacial capacitance is developed, which are essentially related to space charge regions in the Ag_2S-AgI electrode and can be used for a Mott-Schottky analysis for the semiconducting properties of electrode. The Mott-Schottky plot of $1/C_{sc}^2$ against applied potential (E) is shown in **Fig 3**. A straight line with a positive slope $2/e\ \varepsilon\ \varepsilon_o\ N_D$ was observed between +0.2 V to –0.2 V (SSE) indicating *n*-type semiconductor behavior of polycrystalline Ag_2S-AgI membrane. The donor concentration N_D was calculated from the slope using dielectric constant of Ag_2S-AgI. The N_D value of 1:1 electrode is found to in the range of semiconducting material ie, the value obtained is ~ 6 orders of magnitude lower than in metals. This is an important implication for the charge and potential distribution at the semiconductor/electrolyte interface. The Mott Schottky analysis have shown that the present material is *n*-type semiconductor with donor defect concentrations in the range of $7.4\text{x}10^{17}$ / cm^3 and flat band potential is found to be -0.18 (V).It can be observed that 1:1 Ag_2S-AgI electrode showed a Nernstian behavior of 58.7 in the iodide concentration range of $1\text{x}10^{-1}$M to $1\text{x}10^{-6}$M was due to reasonable value of N_D for a polycrystalline material.

Conclusion

A Mott-Schottky analysis of 1:1 Ag_2S-AgI electrode in aqueous electrolytes shows n-type semi-conductivity. The donor defect concentration is of a reasonable order of magnitude for a polycrystalline material.

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