Modeling Transfer of Electrons between Energy States of an Electrolyte and CdS Thin Films using Gerischer Model

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ABSTRACT

A number of models have been developed to describe electron transfer between electrolytes and group II–VI binary semiconductors. In this report, a study was conducted to describe and model electron transfer between an inorganic semiconductor, (i.e. CdS) and a ferric oxidizing/reducing agent [i.e. $K_3Fe(CN)_6/K_4Fe(CN)_6$]. We describe the interfacial electron transfer using the semi-classical theory approaches as described by Marcus and later developed by Gerischer and therefore called Gerischer model as it is applied to heterogeneous electron transfer in a semiconductor - electrolyte interface. CdS thin films were grown by electro-deposition method on the indium tin oxide (ITO) substrates and were used as electrodes. The data collected was used to determine the kinetic constant rates and re-orientation energies as measured in the solutions with different concentration of redox system, $Fe^{+3}/\ Fe^{+2}$. Experiments showed that when concentration of oxidized species increased and causing an increase in $E_{F,redox}^{\circ\ 2}$ activity, the kinetic constant rates decreases inversely. Equally light induced current at 0.0V/Ag was higher when the ratio of the oxidant-reductant (i.e. 2/0.02 and 0.2/0.02) was high. EIS studies revealed that for the two ratios of. 2/0.02 and 0.2/0.02, the difference of current density was comparable to the transfer of the charge carriers for the oxidant-reductant electrolyte at 2/0.02 with respect to 0.2/0.02.

Key words

Fe+3/ Fe+2 Oxidant-Reductant electrolyte; cadmium sulfide; Gerischer model; Indium tin oxide, ITO, ITO/CdS interface, Marcus

6/30/2015 **Source of Support:** Technical University of Mombasa , **No Conflict of Interest:** Declared

INTRODUCTION

Cadmium sulfide which is abbreviated as CdS is a popular inorganic semiconductor that has been studied extensively for solar cells using chemical bath deposition method. It is also one of the most important groups of II–VI semiconductors with a band-gap of 2.4eV which is suitable for many other semiconductor device applications (Wolcott etal, 2009). This study chose CdS particularly because of its interesting behavior; *due to its relatively high absorption coefficients, unique optical properties and ease to growth or deposit* (Gerischer, 1990). CdS thin films have made a break-through in solar cells as a promising candidate for photovoltaic device especially those fabricated on indium tin oxide (ITO) substrates. Many material investigators have made a number of studies on nano-structured semiconductor electrodes (Jia etal, 2006) but only a few have investigated the effect of a few redox electrolytes to improve the performance of research prototype solar cells. The most commonly investigated electrolyte is that of tri-iodide/ iodide (I_3^-/I^-) oxidant-reductant electrolyte couple (Einstein etal, 1935) but little has been done on Fe^{+3}/ Fe^{+2} oxidant-reductant electrolyte system. Although, this tri-iodide/ iodide (I_3^-/I^-) oxidant-reductant electrolyte redox couple works efficiently in most materials tested, it has quite a number of disadvantages (Chiba etal, 2006). It is important to study another redox couple and hence a choice was made on Fe^{+3}/ Fe^{+2} oxidant-reductant electrolyte system using Gerischer's approaches. In 1960, a researcher by the name Gerischer developed a solid-liquid model in which he postulated that charge transfer occur in terms of electronic energies in the solid and energy levels in solution associating it with those of ions (Gerischer, 1990; Appleby, 1974). This model later became suitable and can be applied when analyzing semiconductor electrodes because electron transfers occur through their conduction or valence bands (Nazeeruddin etal, 2001). The work reported highlights theoretical approaches about effect of redox electrolytes in aqueous solvents on the photo-electrochemical behavior of CdS solar cells and demonstrates the behavior of Gerischer's model using CdS/ Fe^{+3}/ Fe^{+2} system. It also describes the interfacial electron transfer reactions using semi-classical theory between bands which was originally developed by Marcus for a donor-acceptor system in homogenous medium (Nazeeruddin etal, 2001) only.

THEORETICAL CONSIDERATIONS ON REDUCTION AND OXIDATION

The process of oxidizing involves the addition of oxygen to a compound with a loss of electrons and it is always accompanied by reduction. Any process in which electrons are added to an atom or ion (as by removing oxygen or adding hydrogen) is called reduction and is also always accompanied by oxidation of the reducing agent. Therefore, considering a simple redox reaction, the Nernst equation for a redox reaction in terms of electrochemical potentials is simplified so as to be expressed as:

$$\mu_{e,redox} = \mu^{\circ}_{e,redox} + kT\ \ln\left(\frac{C_{ox}}{C_{red}}\right) \tag{2.1}$$

where $\mu_{e,redox}$ is the electrochemical potential of electrons in the redox system; C_{ox} is the concentrations of the oxidation species and C_{red} is the concentrations of the reduction species. The electrochemical potential symbolized as $\mu_{e,redox}$ is equivalent to a Fermi level of a redox system, $E_{F,redox}$, The same test reference level is used for a solid electrode and any redox system as demonstrated in equations (2.2) and equation [2.1].

$$\mu_{e,redox} = E_{F,redox} \tag{2.2}$$

In most recent studies involving redox systems, corresponding redox potentials are given based on a natural conventional scale using the Ag/AgCl reference electrode (Memming, 1984; Appleby, 1974). Contrary to this approach, in the Gerischer model that is applied in this report, an electron transfer can occur from an occupied state in the metal or the semiconductor to an empty state in the redox system. This implies that in Gerischer model approach, the rate of electron transfer depends on the density of energy states on both sides of the interface irrespective of solid/liquid/electrolyte states. In a case where an electron transfer from the valence band of a semiconductor to the redox system occurs, the rate of transfer (Gerischer, 1990; Jia etal, 2006; Vanmaekelbergh, 1997) can be given by the expression as:

$$\mathrm{j}_v^- = \mathrm{e}\ \mathrm{k}_v^- \mathrm{N}_v \mathrm{C}_{ox} \tag{2.3}$$

were k_v^- is the rate constant in the valence band and N_v is the density of states in the valence band. This means that, if N_v is the approximate constant, then the ratio of j_v^- / C_{ox} as given in equation (2.4) can be an appropriate criterion to use to manupulate the value of the rate constant in the valence band k_v^-;

$$\mathrm{j}_v^- / C_{ox} = \mathrm{e}\ \mathrm{k}_v^- \mathrm{N}_v \tag{2.4}$$

so as to obtain equation (2.5). Therefore according to equation (2.5), the value of k_v^- will dependent on an exponential expression of redox Fermi ($E^{\circ}_{F,redox}$), the edge of the valence band at the semiconductor-electrolyte junction (E_v^s) and the re-orientation energy of redox (λ) respectively (Gerischer, 1990; Jia etal, 2006; Nazeeruddin etal, 2001). Thus using all this dependant parameters illustrated in equation (2.5), the value of k_v^- as an exponential expression can be written as;

$$k_v^- = \mathrm{k}_0 - \exp\left(\frac{\left(E_v^s + \lambda - E^{\circ}_{F,redox}\right)^2}{4\mathrm{kT}\lambda}\right) \tag{2.5}$$

Using equation (2.5), the accurate constant rate k_v^- as defined by equation (2.5) can only be calculated if the values of λ and the energy difference $E_v^s - E^{\circ}_{F,redox}$ are known. However, if $E_v^s + \lambda = E^{\circ}_{F,redox}$ and is an exact value, then the value of constant k_v^- equals to maximum value of constant rate, k_0. This will estimate the value of k_v^- as a constant and can be done by substituting j_v^- / C_{ox} from equation (2.4) in equation (2.5) and rearranging equations (2.5) using (2.6) and (2.7) as shown below taking the value of a as expressed in equation (2.8) which will finally plot a curve of $\ln k_v^-$ versus $E_{F,redox}^{\circ}{}^2$ according to the equation (2.7).

$$\ln k_v^- = \ln \mathrm{k}_0 - \frac{\left(E_v^s + \lambda - E_{F,redox}^{\circ}\right)^2}{4\mathrm{kT}\lambda} \tag{2.6}$$

$$\ln k_v^- = -\frac{E_{F,redox}^{\circ}{}^2}{4\mathrm{kT}\lambda} + a \tag{2.7}$$

The value of λ can thus be determined from slope. It found to be expressed from this line given from [$\frac{1}{4\mathrm{kT}\lambda}$] and hence the value of a can be expressed as;

$$a = \ln \mathrm{k}_0 - \frac{(E_v^s + \lambda)^2 - 2(E_v^s + \lambda)E_{F,redox}^{\circ}}{4\mathrm{kT}\lambda} \tag{2.8}$$

Many models (Wolcott etal, 2009; Gerischer, 1990; Jia etal, 2006; Nazeeruddin etal, 2001; Dogonadze and Kuznetsov, 1975; Heusler and Schulze, 1975; Appleby, 1974), approximate the value of $4\mathrm{kT}\lambda$ is to be about 0.1eV and this lets λ be easily calculated in the order of 1eV (Wolcott etal, 2009; Nazeeruddin etal, 2001).

EXPERIMENTS

Materials

Pyrex glass slides coated with ITO was used as a substrate. The following reagents and materials were used among other, $Cd(NO_3)_2$, thiourea, NaOH, $K_3Fe(CN)_6/K_4Fe(CN)_6$ all of analytical grade were bought from Merck Suppliers in Nairobi.

Preparations of Solutions

Di-ionized water were used to prepare different concentrations of $K_3Fe(CN)_6$/ $K_4Fe(CN)_6$ solutions as concentrations of Oxidation/Reductant electrolyte solutions. The prepared solutions were of different values of 0.02/0.02, 0.02/0.2, 0.2/0.02, 0.2/0.2 and 2/0.02 as required in set-up.

Cleaning of Substrates

Pyrex glass slides coated with ITO were degreased in nitric acid for 24 hours, washed with detergent, rinsed in di-ionized water and dried in air for 2 hours (Wang etal, 2010) according to…. Pieces of the ITO substrate sheets with an area of 1cm^2 were cut to be used, cleaned with distilled water, acetone and ethanol and finally ultra-sonicated in the isopropanol. They were kept for the Electro-deposition of CdS thin films.

Growth Procedure

Preparation of ITO/CdS electrode: A solution of 0.1M $Cd(NO_3)_2$ was prepared to be used. CdS thin films were grown by electro-deposition on the indium tin oxide (ITO) to create the semiconductor solid. The redox solutions were used as the electrolytes for all other experimental tests. Sulfur was to be oxidized in the alkaline solution at about pH>10 from a solution containing 0.2 M thiourea. A few layers were grown and after electrodepositing of each layer, the surface of electrode was rinsed with distilled water to remove unabsorbed ions. The resulting electrode is denoted as ITO/CdS.

Preparation of redox solutions: Different concentrations of $K_3Fe(CN)_6/K_4Fe(CN)_6$ solutions as concentrations of Ox/Red solutions as follows: 0.02/0.02, 0.02/0.2, 0.2/0.02, 0.2/0.2 and 2/0.02 as shown in the table 1:

Table 1: Concentrations of $K_3Fe(CN)_6/K_4Fe(CN)_6$ solutions

Redox Agent	Concentrations of Samples used				
	A	**B**	**C**	**D**	**E**
$K_3Fe(CN)_6$	0.02	0.02	0.2	0.2	2
$K_4Fe(CN)_6$	0.02	0.2	0.02	0.2	0.02

Procedure for Electro-deposition CdS thin films: Chronoamperometry is an electrochemical technique in which the potential of the working electrode is stepped and the resulting current from faradaic processes occurring at the electrode is monitored as a function of time. Though limited information about the identity of the electrolyzed species can be obtained from the ratio of the peak oxidation current versus the peak reduction current, chronoamperometry generates high charging currents, which decay exponentially with time as any RC circuit. The Faradaic current--which is due to electron transfer events and decays as described in the Cottrell equation **(Cottrel, 1902)**. Cottrell (1958) proposed an alternative dislocation mechanism for the nucleation of cleavage cracks in BCC metals such as ferritic iron. He argued that two dislocations slipping on intersecting (101) planes interact to form a new dislocation with Burgers vector normal to the cleavage plane. The interaction leads to a reduction in dislocation energy so that crack nucleation is easier than in the Zener-Stroh mechanism. Cottrell suggested that fracture by this mechanism would occur when the following criterion is met:

$$\sigma_f \geq \frac{2\mu\gamma}{k_y^s} d^{-1/2} \qquad (2.9)$$

where **d** is the grain size, **μ** is the shear moduls, **γ** is the surface energy, and **k_y** is the Hall-Petch yielding constant and this can apply to energy transitions in thin films. In most electrochemical cells this decay is much slower than the charging decay and chronoamperometry gives a better signal to noise ratio in comparison to other amperometric technique (Wolcott etal, 2009; Gerischer, 1990; Einstein etal, 1935). Chronoamperometry technique or method was used to electro deposit the cadmium and sulfur for 1 min separately on the ITO substrates as follows: at the first Cd^{+2} were reduced on the ITO using in solution containing 0.1M $Cd(NO_3)_2$. Equally sulfur was oxidized in these alkaline solutions at a pH>10 containing 0.2 M thiourea. After electrodepositing of each layer, the surface of electrode was rinsed with distilled water to remove unabsorbed ions. The resulting electrode is denoted as ITO/CdS. This UPD procedure was repeated 10 times to achieve 10 layers of CdS.

Techniques and Instruments

Test Instruments: All electrochemical measurements were carried out in a conventional three-electrode cell powered by a μ-Autolab-potentiostat/ galvanostat and a frequency response analyzer at the University of Cape Town, at the School of Material Science laboratory.

Testing Techniques: A frequency range of 100 kHz –10 MHz was used with modulation amplitude of 5mV. This employed an Electrochemical Impedance spectroscopy (EIS). The impedance studies were carried out in open circuit potential (Dogonadze etal, 1968) and later fitted in by **Zview3.1** software. The Pyrex glass coated ITO was set as a working electrode while graphite was set as a counter. Finally, Ag/AgCl electrode was set as a reference electrode (Appleby, 1974; Memming, 1984). A bulb of 100W made from tungsten lamp was set as uniform light source.

RESULT AND DISCUSSION

The figure 1 shows a plot of the relationship of the Ox/Red reagents used and labeled as sample A, B, C, and D in that order . The results obtained were expressed as curves obtained from the **Zview3.1** software. Shown in table 2 below is the results of the simulation where ***a***, is related to reduction of H_2O at -1.8V/Ag/AgCl.

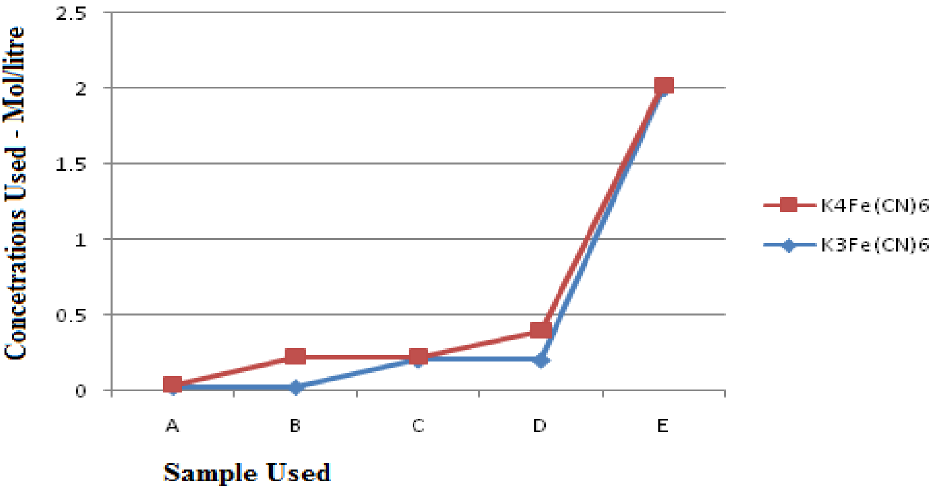

Figure 1: Relationship of the Ox/Red reagents and samples

It can be noted that from this table that + 0.5 to - 0.7V, the oxidation and reduction peaks plotted relates to the redox system of Fe^{+3}/Fe^{+2} . The curves in the figure 2 demonstrate the effect of the concentration of Fe^{+3}/Fe^{+2} redox system and how they affect the reduction peak current of Fe^{+3}, I_P. As it can be noted from the third column in Table 2, the highest reduction peak current is related to the redox electrolyte of Fe^{+3}/Fe^{+2} with 2/0.02 ratio as shown in figure 2. The simultaneous increase in the values of $E_{F,redox}$ and their corresponding Fe^{+3} concentrations confirm the positive effect and effectively increases the value of the current I_P. Another cathodic current initiated at -0.7V/Ag/AgCl as a reference electrode continues to increase up to the more negative potentials. These negative potentials are related to the reduction of H_2O (Vanmaekelbergh, 1997) and this implies that the reduction of Fe^{+3} simultaneously accompanies the reduction of water in this same region because the reduction of current increases as Fe^{+3} concentration increases.

Table 2: Kinetic constant rate from approximated relation by substituting j_v^- / C_{ox} instead of k_v^-

$Ox / Red (M)$	$E_{F,redox}$ (V)	$I_p (A)\times10^4$	$E^{\circ}_{F,redox}{}^{2}$	$^{a}j_v^-$ (A)	$^{a}j_v^- / C_{ox}$	$^{a}\ln k_v^-$
0.02/0.02	+0.58	6.93	0.49	-0.013	0.65	-0.43
0.02/0.2	+0.52	23.5	0.59	-0.012	0.6	-0.51
0.2/0.02	+0.64	7.7	0.68	-0.017	0.085	-2.46
0.2/0.2	+0.58	20	0.49	-0.021	0.105	-2.25
2/0.02	+0.74	50	0.77	-0.026	0.013	-4.34

This reduction observed on the CdS thin film surface can be reasoned from the CdS thin film band structure (Vanmaekelbergh, 1997) and how it interacts with the potential of Fe^{+3} / Fe^{+2} redox agent. Therefore, to analyze these curves, the position of the energy bands at the surface of CdS thin films in aqueous solutions must be taken into account (Wolcott etal, 2009). This approach confirms the references obtained in the valence and conduction band position in CdS in the dark are placed at +0.7 and -1.7V/Ag/AgCl, respectively (Wolcott etal, 2009; Gerischer, 1990; Wang etal, 2010; Dogonadze and Kuznetsov, 1975) and the electrochemical standard potential of Fe^{+3} / Fe^{+2} obtained was 0.58V/Ag/AgCl. Figure 2 and table 2 concurrently show that the reduction of Fe^{+3} ions is initiated at +0.5V/Ag/AgCl and therefore accordingly, the valence band position of CdS at + 0.7V/Ag/AgCl, and the reduction current of Fe^{+3} when compared, occur in the valence band of CdS due to vicinity of energy levels. It was also observed that by increasing of the concentration of the oxidized species (Fe^{+3}) from 0.02 to 2 Molar, the values of $E_{F,redox}$ changes from 0.58 to 0.74V/Ag/AgCl respectively and result into a redox Fermi level of Fe^{+3} / Fe^{+2} which equally approximates to the theoretical energy level of CdS valence band which causes a reduction current in this region.

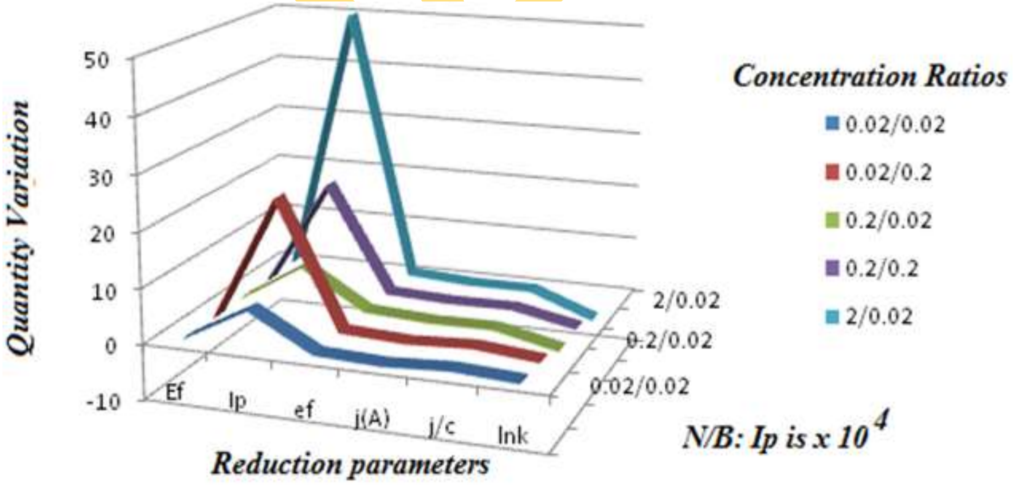

Figure 2: plot of concentration and reduction parameters

A similar observation (Dogonadze and Kuznetsov, 1975; Vanmaekelbergh, 1997; Stimming and Schultze, 1979) has been obtained for H_2O though lower. Increasing the oxidized species (Fe^{+3}) from 0.02 to 2 changes of the value of $E_{F,redox}$ from 0.58 to 0.74V/Ag/AgCl reference electrode. This causes the reduction current of H_2O from -0.013 to -0.026A at -1.8V/Ag/AgCl respectively (Jia etal, 2006; Chiba etal, 2006; Nazeeruddin etal, 2001) and this change results into a change of $\ln k_v^-$ from -0.43 to - 4.34 which implies that the rate constant is reduced or decreased. When the concentration of oxidized species increases, $E^{\circ}_{F,redox}{}^2$ increase too and the kinetic constant rate decreases inversely. This is in good agreement with equation (2.7) that increase of $E^{\circ}_{F,redox}{}^2$ causes decrease of the $\ln k_v^-$ because of negative sign of $E^{\circ}_{F,redox}{}^2 / 4kT\lambda$ .The re-orientation energy of redox (λ) from slope of this line is obtained as 0.7eV. This value is within the acceptable limits of Gerischer model (Gerischer, 1990). Using the theoretically approach (Einstein etal, 1935; Dogonadze and Kuznetsov, 1975; Dogonadze etal, 1968) and current difference demonestrated in out theory part 2.0 and an applied potential in the dark and light conditions, a lot of concern can be raised to the light induced processes (Wolcott etal, 2009). Under applied overvoltages and in the dark, the cathodic current follow equation (2.9) and using j_0 as an exchange current, j_v^- can then be expressed as;

$$j_v^- = - j_0[\exp(-\frac{e\eta}{kT}) -1] \qquad (2.9)$$

It is therefore noted that the value of j_v^- in the dark condition is only dependent on applied overvoltage which can be symbolized as, η . According to the plot shown in figure 2, the value of j_v^- at 0.0V/Ag/AgCl reference electrode in the dark and light conditions imply effective higher light induced current. This unique phenomenon demonstrates and equally admits the existence of a relationship between the Fermi Redox Energy and Band Energy position (Di Quarto etal, 1981; Wolcott etal, 2009; Gerischer, 1990) in especially in CdS tested in this work. A Nyquist spectra plot (Wang etal, 2010; Boddy etal, 1968; Memming, 1984) can be equally be plotted so that that curve will show the relationship of CdS thin film at the OCP in the dark and under light conditions for the used concentrations of redox electrolytes. The highest values of j_v^- will be demonstrated by the figure 3. This work can also use a spectra fitted into **Randles** equivalent circuit and it will show a high frequency region, in which the value of R_s would be related to the resistance of the CdS thin film in different concentrations of redox electrolyte.

When calculated, the diameter of semicircle (R_{ct}) was found to be related to resistance of charge carriers in CdS semiconductor. The decrease in value of R_{ct} at light condition (***not shown in any of the curves or figure in this report***) was due to the increase of the charge carriers such as electron in n-type semiconductors present in CdS thin films (Memming, 1984; Appleby, 1974).

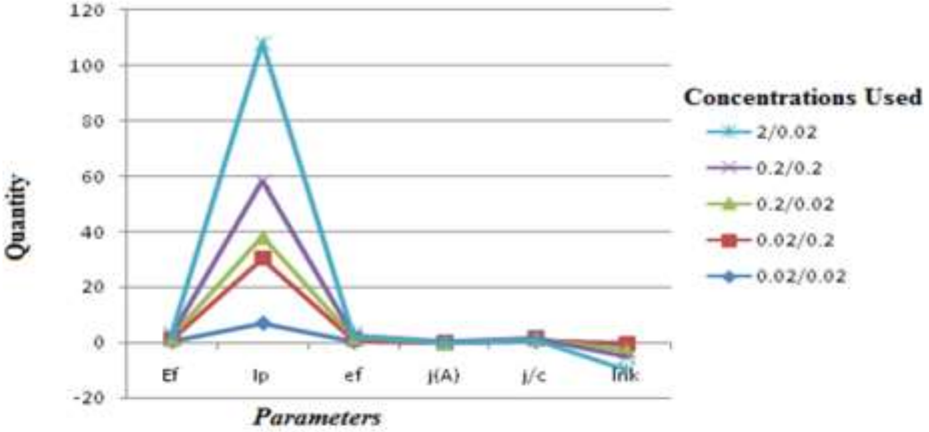

Figure 3: CdS thin film at the OCP under dark and light conditions for the two concentrations of redox electrolyte

This demonstrated that the difference of the current density was comparable to the transfer of the charge carrier for redox electrolyte. This was confirmed from the difference of R_{ct} values on the I-V plots and the value of the charge transfer resistance is therefore related to the current density j_v^- reversely (***not shown in any of the curves or figure in this report***).The value of R_{ct} in the redox electrolyte 2/0.02 was obtained to be near its value in the redox electrolyte 0.2/0.02 when the CdS thin film was in darkness. The values of R_{ct} differ remarkably when under illumination and can be plotted in Bode phase plots which may also show a positive relationship if Nyquist plots in different concentrations of redox electrolyte are plotted.

CONCLUSION

A study was conducted to demonstrate the electron transfer between electrolytes and a semiconductor of CdS. Chronoamperometry technique was employed to electrodeposit cadmium and sulfur separately on ITO to form ITO/CdS as a semiconductor interface and was tested against the ITO/CdS/ $K_3Fe(CN)_6/K_4Fe(CN)_6$ interface. The CV measurements of the ITO/CdS in the redox electrolyte with different concentration of Fe^{+3}/Fe^{+2} was done and showed that the highest reduction current was related to the redox electrolyte of Fe^{+3}/Fe^{+2} with 2/0.02 ration and $E_{F,redox}$ = 0.74eV. The valence band position of CdS and the reduction current of Fe^{+3} were found to occur in the valence band. Experiment showed that when concentration of oxidized species and $E^{\circ}_{F,redox}{}^{2}$ increase, the kinetic constant rate decreases inversely. EIS studies showed that the difference of the current density was comparable to transfer of the charge carrier for redox electrolyte 2/0.02 with respect to 0.2/0.02. It was concluded that manipulating CdS/Fe^{+3}/Fe^{+2} can improve and optimize the design of CdS thin film solar interface.

ACKNOWLEDGMENTS

The authors are gratefully acknowledging Technical University of Mombasa for providing financial support to facilitate Electrochemical Impedance spectroscopy tests (EIS), University of Nairobi for allowing the authors to use their test instruments, the Physics laboratory technicians of Maasai Mara University and Kenyatta University for providing the simulation software.

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