CHAPTER II

THEORY

Dye-sensitized solar cell (DSSC)

The dye sensitized solar cell (DSSC) mainly consists of light sensitive dyes, porous layer of TiO_2 (wide band gap semiconductor), redox electrolyte, front and back electrodes made of transparent conducting oxide (FTO). At the heart of the system is a mesoporous oxide layer composed of nanometer-sized particles which have been sintered together to allow for electronic conduction to take place. The material of choice has been TiO_2 (anatase) although alternative wide band gap oxides such as ZnO, and Nb_2O_5 have also been investigated.

The principle of DSSC is the photoexcitation of dye resulting in electron injection into the conduction band of the metal oxide (MO), hole injection into the electrolyte, and gets reduced as shown below (Thavasi et al,. 2009):

$$\text{Dye}^{+\,-} + \text{MO} \xrightarrow[\text{electron injection}]{} \text{Dye}^{+} + \text{MO}^{-} \tag{2.1}$$

Redox species, usually comprises of iodide/triiodide redox couple, in the electrolyte transport the holes from the oxidized dye to the counter electrode. In the absence of redox species, the injected electrons from excited state of dye undergo recombination with oxidized dye, instead of iodine.

$$\text{Dye}^{+} + \text{MO}^{-} \xrightarrow[\text{recombination with dye}]{} \text{Dye} + \text{MO} \tag{2.2}$$

The redox electrolyte prevents the reduced dye recapturing the injected electron by donating its own electron and thus regenerates the reduced dye.

$$\text{Dye}^{+} + 2\text{I}^{-} \xrightarrow[\text{dye regeneration}]{} \text{Dye} + \text{I}_2^{-} \tag{2.3}$$

The oxidized iodide is then regenerated by the triiodide at the counter electrode, with the electrical circuit being completed via electron migration through the external load.

$$I_2^- + MO^- \longrightarrow 2I^- + MO \tag{2.4}$$

iodide regeneration

Back electron transfer from metal oxide into the electrolyte is however the primary and predominant recombination pathway in DSSC, which lower the conversion efficiency.

$$I_2^- + MO^- \longrightarrow 2I^- + MO \tag{2.5}$$

recombination with electrolyte

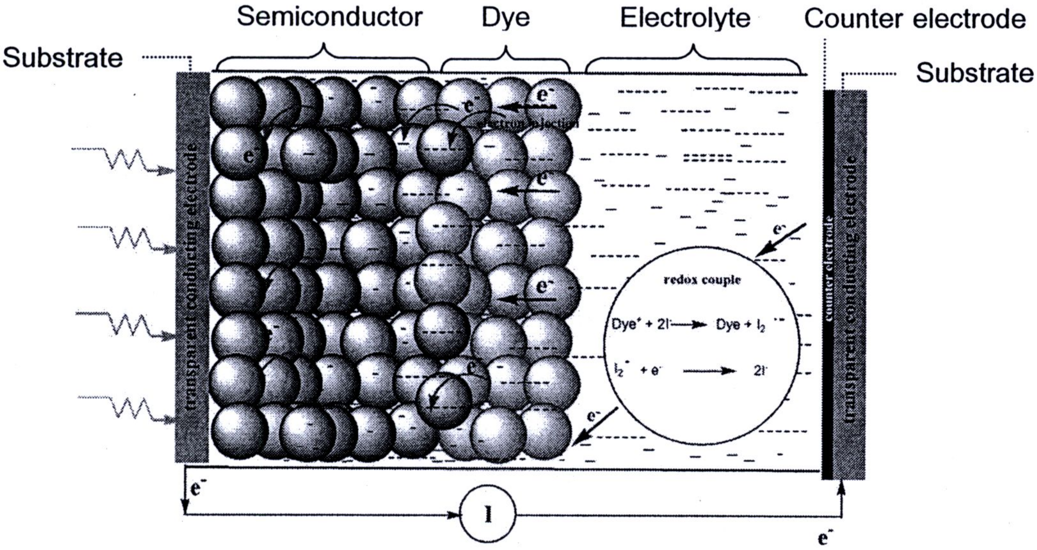

Figure 2.1 Schematic diagram of dye sensitized solar cells (Thavasi et al., 2009)

The performance of each components is crucial and have been designated using the parameters: open-circuit voltage Voc, fill factor FF and short circuit current density Jsc and expressed as efficiency (η) using the equation:

$$\eta = \frac{V_{OC} J_{SC} FF}{P_{in}} \quad \text{and} \quad FF = \frac{I_{max} V_{max}}{J_{SC} V_{OC}}$$

Whereas Voc, is the maximum voltage obtained at zero current.

Jsc, the shot circuit current is the maximum current obtained under less resistance (short circuit) condition.

P_{in} is the solar radiation intensity.

I_{max} and V_{max} are the maximum current and maximum voltage, respectively.

2.1 Components of DSSC

2.1.1 Photosensitized

The best photovoltaic performance both in terms of conversion yield and long-term stability has so far been achieved with polypyridyl complexes of ruthenium and osmium. Sensitizers having the general structure ML2 (X) 2, where L stands for 2,2'-bipyridyl-4,4'-dicarboxylic acid M is Ru or Os and X presents a halide, cyanide, thiocyanate, acetyl acetonate, thiacarbamate or water substituent, are particularly promising.

The amount of the sensitizer molecules available for light harvesting and charge injection are important upon adsorbing dye onto the metal oxide. Dye molecules are to be oriented on the surface of metal oxide with attachment functionalities of the molecule. Orientation reduces the covering area per adsorbed molecule, providing a more compact and packed arrangement of the dye molecules, which allow for more adsorption dye of molecules. The rate constant for the migration of the excited energy would depend on the relative orientation of the donor and acceptor moieties. However, this is no longer possible if the dye is adsorbed as aggregates. Problem of poor electron transfer to the metal oxide conduction band would be arisen if dyes are aggregated that results in an unsuitable energetic position of the LUMO level. Lower current density could be resulted by poor injection efficiency, due to unfavourable binding of dye onto the metal oxide surface. The orientation of the molecule on the metal oxide surface is characterized by the anchoring group present in the dye (Rochfoed et al., 2007). Anchoring groups of dye to the semiconductor surface is the most decisive factor help in bringing the relative orientation of energy level of donor and acceptor during the attachment on the metal oxide and increase injection efficiency. Thus, the ruthenium complex *cis*-$RuL_2(NCS)_2$, known as N3 dye, shown in Figure 2.2 has become the paradigm of heterogeneous charge transfer sensitizer for mesoporous solar cells.

The fully protonated N3 has absorption maxima at 518 and 380 nm, the extinction coefficients being 1.3 and 1.33 × $10^4 M^{-1} cm^{-1}$, respectively. The optical transition has metal-to-ligand charge transfer (MLCT) character: excitation oft the dye involves transfer of an electron from the metal to the p* orbital of the surface anchoring carboxylated bipyridyl ligand from where it is released within femto- to picoseconds into the conduction band of TiO_2 generating electric charges with unit quantum yield (Grätzel., 2003).

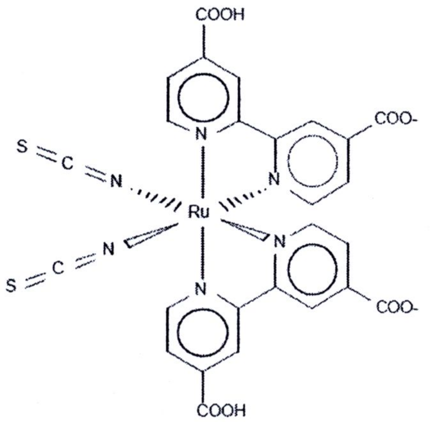

Figure 2.2 Chemical structure of the N3 ruthenium complex used as a charge transfer sensitizer in dye-sensitized solar cells. (Gratzel., 2003)

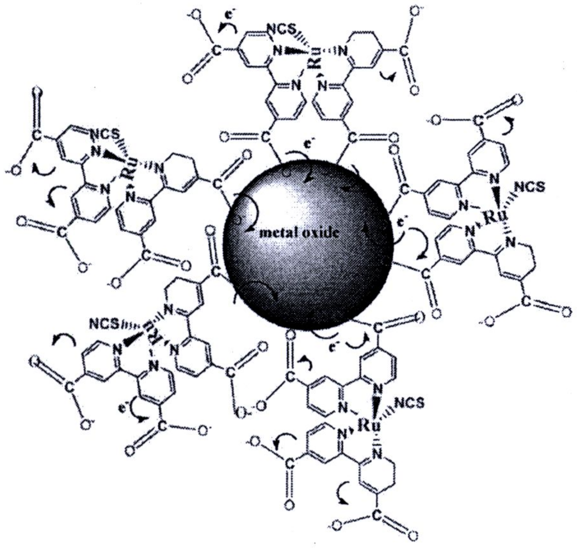

Figure 2.3 Inefficient electron injection into metal oxide arises from misalignment and higher degree of protonation in N3 dye. (Thavasi et al., 2009)

N3 dye has two bipyridine ligands and four carboxyl groups in its structure and adsorption may occur via several modes viz. protonation of one or more of all the four carboxyl groups (Nazeeruddin et al., 2003), which results in difference in their energy levels that in turn lead to differences in their electron injection efficiency. For example, the fully protonated N3 dye, while possessing an excellent light-harvesting capability, shows poor electron injection efficiency due to the misalignment of the dye on TiO_2 (Figure 2.3) (Nilsing et al., 2007).

2.1.2 TiO_2 electrode film

Nano-porous TiO_2 thin films have been widely used as the working electrodes in dye-sensitized solar cells (DSSC). In DSSC, titanium dioxide (TiO_2) is one of the most promising materials used for nano-porous thin film due to its appropriate energy levels, dye adsorption ability, low cost, and easy preparation (Hsiue , 2010).

Titanium dioxide (TiO_2) is a wide band gap (~3.2 eV for the anatese phase) semiconductor material which has been under extensive investigations due to its applications in a variety of fields such as photoelectrolysis (Mishra et al., 2003), photocatalysis (Yu et al., 2001) comprise dye sensitized solar cells (Ko et al., 2005). TiO_2 has 3 crystalline forms: anatase, rutile and brookite. Many important applications of TiO_2 depend on its structural and optical properties. The anatase phase gained much attention due to its more active surface chemistry and smaller particles for more dye adsorption, which has better response with ultraviolet photons is used for photocatalysis (Yu et al., 2001). Anatase is metastable and can be transformed irreversibly to thermodynamically more stable and condense rutile phase at higher temperature. The rutile phase has good stability and high refractive index .which makes it suitable for protective coatings on lenses (Takikawa et al., 1999). Rutile to anatase transformation occurs in the temperature range 700-1000°C depending on the crystallite size and impurity content. The band gap energies for anatase and rutile have been estimated to be 3.2 and 3.0 eV, respectively.

Titanium oxide films have been made by a variety of techniques such as e-beam evaporation, magnetron sputtering technique, anodization, chemical vapour deposition (CVD) and sol gel technique. Among the different methods for the preparation of thin TiO_2 layer, sol-gel technique is widely used because of its low processing cost, simplicity and ability to produce thin and uniform films on large area substrates (Mathews et al., 2009).

The sol-gel conventional method uses the hydrolytic route, which involves the initial hydrolysis of the alkoxide precursor followed by continual condensations between the hydrolysed particles forming the gel. The hydrolysis and the polycondensation of titanium alkoxides proceed according to the following scheme (Harizanov et al., 2000):

$$\text{M-O-R} + \text{H}_2\text{O} \longrightarrow \text{M-OH} + \text{R-OH} \qquad \text{Hydrolysis reaction} \tag{2.6}$$

$$\text{M-OH} + \text{HO-M} \longrightarrow \text{M-O-M} + \text{H}_2\text{O} \qquad \text{Water condensation} \tag{2.7}$$

$$\text{M-O-R} + \text{HO-M} \longrightarrow \text{M-O-R} + \text{R-OH} \qquad \text{Alcohol condensation} \tag{2.8}$$

Then, M substitute the semiconductor material sach as Si, Zr, Ti, Al, Sn or Ce
OR substitute the alkoxyl group

2.1.3 Counter electrode performance

Solar cell studies employ usually a Fluorine dope tin oxide (FTO) as the conducting glass electrode. Such electrodes are known to be poor choice for efficient reduction of triiodide. To reduce the overvoltage losses, a very fine Pt-layer or islands of Pt is deposited on to the conducting glass electrode. This ensures high exchange current densities at the counter-electrode and thus the processes at the counter electrode do not become rate limiting in the light energy harvesting process (Kalyanasundaram et al., 1998).

2.2 Structure and operation principles of dye-sensitizer solar cell

The primary processes in dye-sensitized solar cells. At the heart of the system is a nanocrystalline mesoporous TiO_2 film with a monolayer of the charge transfer dye attached to its surface. The film is placed in contact with a redox electrolyte or an organic hole conductor. Photoexcitation of the sensitizer dye (process (1) in Figure 2.4), the electrons are injected from the excited sensitizer dyes into the conduction band (CB) of the semiconductor film (electron injection) (process (2) in Figure 2.4). The injected electrons recombine with the oxidized sensitizer dyes (recombination). This recombination process competes with the regeneration of the oxidized sensitizer dyes by the redox mediator molecules (rereduction). The electrons can be transported in the semiconductor film as the conducting electrons. The conducting electrons can react with the redox mediator molecules or with molecules in the solution during transport, before reaching the back contact electrode (leak reaction). Finally, the remaining electrons flow into the external circuit (Katoh et al., 2004).

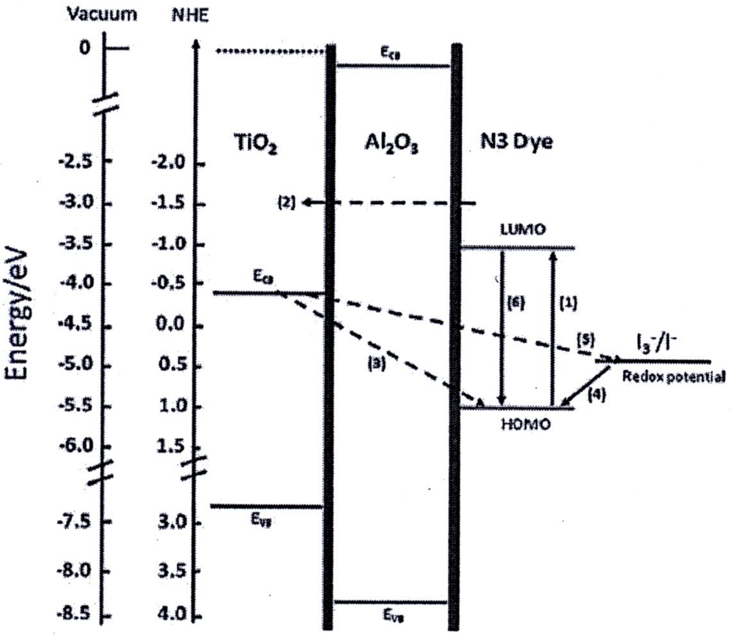

Figure 2.4 Schematic diagram of band structure including interfacial charge-transfer processes occurring at TiO_2|dye|electrolyte interface in dye-sensitized solar cells. (Ganapathy et al., 2010)

Efficient operation of a DSSC device relies on minimization of the possible recombination pathways occurring at the TiO_2|dye|electrolyte interface to allow efficient charge transport through the TiO_2 porous layer and subsequent charge collection at the device contacts. The energy band structure at the TiO_2|dye interface where charge separation processes take place in a DSSC with photon illumination is illustrated in Figure 2.4. There are two possible recombination losses to consider. The photo-generated electrons may recombine either with oxidized dye molecules (process (3) in Figure 2.4) or with the oxidized redox couple (process (5) in Figure 2.4); the latter reaction is thought to be particularly critical to the device performance. In order to reduce the recombination, many groups have proposed device architectures that include the use of insulating polymers (Gregg et al., 2001), high band-gap semiconductor metal oxides like ZnO and Nb_2O_5. Also the use of insulating metal oxides such as $CaCO_3$, $BaTiO_3$, MgO and Al_2O_3 between the TiO_2 and the dye interface has been attempted.