Development of Dye Sensitized Solar Cell Based on Polymer Gel Electrolyte with Improved Efficiency

ABSTRACT

Dye sensitized solar cells (DSSCs) have emerged as a low-cost option to the more expensive conventional silicon based photovoltaic devices. However, the long-term stability is one of the recurring problems associated with DSSCs. The leakage of the volatile liquid organic solvent in the liquid electrolyte affects the stability of DSSCs. The prime motivation of this research work is to improve the stability of the traditional DSSCs by replacing the liquid electrolyte with various polymer gel electrolytes (PGEs) without compromising its efficiency. In this research, different PGEs based on poly(methyl methacrylate) (PMMA) polymer matrix incorporated with various additives like polyaniline nanotubes (PAniNTs), carbon black (CB) and carbon dots (CDs) are developed to fabricated durable quasi-solid-state DSSCs. Platinum (Pt) is the most popular counter electrode material for DCCSs, but its high price increases the overall cost of the cell. This thesis also emphasizes on the development of alternative graphene based counter electrode material (polyaniline nanotube/reduced graphene aerogel (PAniNT/rGOA)) as Pt-free counter electrode for quasi-solid-state DSSCs, with photovoltaic parameters comparable to those of DSSC fabricated with Pt counter electrode. Chapter-wise summary of the work is given below:

Chapter 1: General Introduction.

This chapter deals with the general introduction which comprises motivation and background of the present research work. All the components of a DSSC (semiconductor, dye molecules, electrolyte components and counter electrode) and their role in the performance of a DSSC are explained in details in this chapter. The working mechanism of the photovoltaic process occurring in a DSSC under illumination of light is also included. This chapter also illustrates all the essential properties associated with the components of a DSSC that are required to obtain maximum possible photoconversion efficiency. A detailed discussion about the properties of the polymer host material is provided and the suitability of PMMA as a polymer host is explained. Moreover, the role of the additives or fillers (e.g., PAniNTs, CB and CDs) in the PGEs is also explained. DSSCs are usually fabricated with the expensive Pt counter electrode. However many low-cost carbon based catalysts are being developed to replace Pt for reducing the cost. Alternative counter electrode materials like PAniNTs and graphene are reviewed.

Chapter 2: A Highly Stable and Efficient Quasi-Solid-State Dye Sensitized Solar Cell Based on Poly(methyl methacrylate)/Polyaniline Nanotube Gel Electrolyte.

This chapter introduces a gel electrolyte based on poly(methyl methacrylate)/polyaniline nanotube (PMMA/PAniNT) with LiI/I_2 as the redox couple, prepared in a solvent mixture of N-methyl 2-pyrrolidone (NMP) and acetonitrile. Different amounts of PAniNTs (0.15, 0.20, 0.25 and 0.30 weight percentage (wt%)) are used to optimize the ionic conductivity of the PGEs. A series of DSSCs are fabricated employing the foresaid gel electrolytes with different wt% of PAniNTs. The optimized system exhibits an open-circuit voltage (V_{OC}) of 0.75 V, short-circuit current density (J_{SC}) of 9.80 mA cm^{-2}, fill factor (*FF*) of 0.68 and photoconversion efficiency of 5.11% under irradiation of 100 mW cm^{-2} simulated sunlight with air mass 1.5. The electrochemical impedance spectroscopy (EIS) is used to study the charge transfer processes occurring inside the DSSCs under irradiation. The increment of PAniNTs in the PMMA based gel electrolytes reduces the charge transfer resistance at the photoanode/electrolyte interface (R_{CT}) and the counter electrode/electrolyte interface ($R_{CT,Pt}$), resulting in enhancement of the device efficiency. The long-term stability study of the DSSCs shows that the PMMA/PAniNT gel electrolyte based DSSC has commendable durability as compared to the device fabricated with liquid electrolyte.

Chapter 3: A Highly Stable and Efficient Quasi-Solid-State Dye Sensitized Solar Cell Based on Poly(methyl methacrylate)/Carbon Black Polymer Gel Electrolyte with Improved Open-Circuit Voltage.

This chapter introduces an efficient and durable DSSC fabricated with a poly(methyl methacrylate)/carbon black (PMMA/CB) based PGE. The added CB improves the ionic conductivity of the PGEs. The optimized DSSC with 0.57 wt% of CB in PMMA polymer matrix exhibits the highest photoconversion efficiency of 5.52 % with J_{SC} value of 12.43 mA cm^{-2}, V_{OC} value of 0.766 V and *FF* value of 0.58. A significant enhancement of V_{OC} is observed in the DSSCs fabricated with PGEs in comparison to the DSSC employing liquid electrolyte. The role of PGE in the enhancement of the V_{OC} is elucidated by analyzing the capacitance (non-faradic processes) values at the interface of the photoanode and the PGE, computed from the data obtained from EIS study. The improvement of J_{SC} in the DSSCs with increasing content of CB is clarified from the lower recombination kinetics (*J-V* characteristics at dark conditions), lower lifetime of the electrons at the photoanode, and lower resistances (R_{CT} and $R_{CT,Pt}$) of the DSSC employing PGE with CB in contrast to the DSSC employing PGE without CB. Additionally, the fast diffusion coefficient of triiodide ions in the PGE with CB also supports the enhancement of the magnitude of the J_{SC} values. Furthermore, the study of long-term stability shows that after 1000 h of testing the optimized DSSC fabricated with PGE with 0.57 wt% of CB retains the J_{SC}

value at 83% of the initial performance exhibiting significant long-term stability in comparison to the DSSC fabricated with liquid electrolyte.

Chapter 4: Effect of Photoluminescent Carbon Dots on the Efficiency of Dye Sensitized Solar Cell with Poly(methyl methacrylate) Based Polymer Gel Electrolyte.

In this chapter a highly efficient and stable quasi-solid-state DSSC fabricated using poly(methyl methacrylate)/carbon dot (PMMA/CD) is introduced. From the UV-visible and photoluminescence spectra of the CDs, it is observed that they emit green light which coincides with the absorption range of the ruthenium dye, enhancing the performance of the DSSC by broadening the range of absorbed light. The electrolyte is mixed with an optimum amount of CDs to prepare the PGE comprising PMMA as the polymer matrix. DSSCs are tested using *J-V* characteristics and impedance spectroscopy under irradiation of light. DSSC fabricated with 0.14 w/v% CD shows 6.05% photoconversion efficiency with J_{SC} value of 9.55 mA cm^{-2}, V_{OC} value of 0.892 V and *FF* value of 0.70, which is more than a two-fold increase in efficiency in comparison with a device fabricated without CDs (2.83%). Simultaneously, remarkable enhancement is achieved in the V_{OC} and J_{SC} values due to the higher number of free electrons in the conduction band of the dye molecules in presence of CDs in the PGE.

Chapter 5: Polyaniline Nanotube/Reduced Graphene Oxide Aerogel as Efficient Counter Electrode for Quasi-Solid-State Dye Sensitized Solar Cells.

A highly efficient graphene based counter electrode for DSSC, polyaniline nanotube/reduced graphene oxide aerogel (PAniNT/rGOA) is presented in details in this chapter. The aerogel, prepared via an organic sol–gel route, having a high surface area of 294.73 $m^2 g^{-1}$ exhibits excellent electro-catalytic activity towards the reduction of triiodide ions in the electrolyte. The catalytic activity of the aerogel based electrodes is manifested with cyclic voltammetry based analyses. The reversible behavior of the cyclic voltammograms for 100 cycles ascribes the stability of the counter electrode. Additionally, the comparable exchange current density of the aerogel counter electrode (computed from the Tafel plots) with Pt counter electrode supports its catalytic activity of reduction of triiodide ions. Electrochemical impedance analyses and *J-V* plots are employed to gauze the photovoltaic performance of the DSSCs fabricated with PAniNT/rGOA counter electrode. The thickness of the counter electrode is a crucial factor that affects the performance of the DSSC. The thicker film offers more surface area for electro-catalytic reduction reaction whilst increasing the charge and mass transport resistances simultaneously. At an optimum PAniNT/rGOA electrode film thickness of 8.68 µm, a power conversion efficiency of 5.47% is achieved from the DSSC employing a PGE of PMMA with 0.57 wt% CB. In addition, an improvement of V_{OC} value is observed due to the capacitance involved at the electrolyte/electrode interface. Moreover, the optimized quasi-solid-state DSSC

fabricated with the PAniNT/rGOA counter electrode employing PMMA based PGE with 0.57 wt% CB exhibits significant long-term stability by retaining 92% of the initial current.

Chapter 6: Conclusion and future scope.

The chapter-wise concluding remarks, major findings and future scopes from this research work are summarized in this chapter. The key outcome of this research work is that the transparent, low-cost PMMA has an immense potential to become one of the polymer host materials for devising a durable PGE based DSSC. The carbon based materials like carbon black and carbon dot, and conducting polymers like polyaniline nanotubes improve the electrochemical properties of a PMMA based PGE when added as additives. These additives significantly improve the efficiency of DSSC. PAniNT/rGOA could replace Pt as a counter electrode in DSSC.