CHAPTER 5
Conclusions and future aspects

Salient Conclusions:

The future energy demands can’t be fulfilled with the depleting fossil fuels or non renewable energy resources, the one and only way to get out of this energy disaster is by the utilization of renewable resources especially solar energy. Solar energy has the potential to fulfil the global energy requirements; but lower efficiency and higher costs are the two main factors which prevent their access to the common man. Currently solar panels work in conjunction with a storage unit to provide effective energy storage for “offline use” and so the price of the combined system is too high to be afforded by common people. The goal of this PhD study is the design and development of a single integrated module which is capable of simultaneous photo energy generation and storage; by which both cost and size can be reduced. The outstanding challenge for direct solar energy storage is to invent a device incorporating both photovoltaic and storage functions in a single cell structure. This thesis work is a concerted effort in this direction; we have progressively evolved a novel DSSC-supercapacitor integrated structure [forerunner to this work: Mini P A et al, Progress in Photovoltaics 2011] that can fulfil the above requirement. The work was further extended for the development of different supercapacitor storage systems. Finally we integrated the best storage system with the DSSC and the performance was studied. The major conclusions drawn from this research work are detailed in various chapters and outlined as below:
Conclusions….

➤ The first chapters proved the concept of novel integration of a thin film device combining a photovoltaic (PV) and a dielectric capacitor wherein both are capable of independent operation as well as combined operation. The initial capacitor chosen for the integration was ZrO\(_2\) based dielectric capacitor with which we could show the concept, but efficiency of storage was poor. We summarized that if the integration scheme can be adequately configured, the integrated device has the potential to replace conventional PV’s and provide a more cost effective system that may reduce dependence on external batteries or other storage systems. This was the motivation for our subsequent studies.

➤ Further we directed our study to optimize of the photovoltaic layers and the dielectric capacitor layers to improve the separate efficiencies of the two components to derive maximum output as useful work. The role and significance of different layers of DSSC is discussed and we could develop a DSSC with efficiency maximum of 3.6% and a nano-zirconia based dielectric capacitor with capacitance of 55 µF/cm\(^2\).

➤ The succeeding section discussed the device physics such as how the flow of current from solar cell to capacitor gets affected by the interfacial barrier or Schottky barrier between Ti metal and nanostructured TiO\(_2\) layer. We determined the barrier to be lower than the Voc of the solar cell (minimum 0.26 V) and overcoming this barrier is required for the unimpeded flow of charges from solar cell to nanostructured capacitor.

➤ We developed two nano dielectrics by the hydrothermal route: ZrO\(_2\) and BaTiO\(_3\) for the development of dielectric capacitor. Final part of this chapter showed the integration of nano dielectric capacitor with DSSC and its performance as a single module was studied. The nano dielectrics gave more consistent and controlled layers for capacitor development but the capacitance, energy density is not high enough to use them for practical storage applications.
- Normal capacitor is not a good option for high energy storage application; so super capacitor having moderately high energy and power density would be a suitable candidate for making an integrated system. High performance super capacitive hybrid electrodes were synthesized with composite materials made of Graphene/polypyrrole (Ppy) and Graphene-PEDOT composites. Graphene/Ppy yielded high values of specific capacitance of 1510 Fg⁻¹, area capacitance of 151 mFcm⁻². Graphene-PEDOT composite electrodes show median specific capacitance of 1410 F g⁻¹ and median area capacitance of 199 mF cm⁻². The composite electrode also showed better electrochemical stability compared to pristine polymer. The composite electrode nano-morphology maximizes the faradiac interaction sites for the hybrid supercapacitor electrode and yields high electrochemical capacitance. The graphene/Ppy system showed good energy and power density falling centrally in the ragone plot for supercapacitors.

- To overcome some of the limitations of graphene/polymer systems, we developed another set of super capacitive energy storage systems with chemically modified carbon nanotube (CNT) and graphene (with metal oxide (NiO)). These electrodes showed good stability, very high area capacitance (upto 800 mF/cm²). Symmetric capacitor was constructed with both the systems and these showed an operating voltage of 2-2.3 V in aqueous KOH electrolyte. The computed energy and power density was far higher than graphene/polymer systems.

- A symmetric capacitor constructed with composite electrode of PPY and CNT in organic electrolyte showed area capacitance of 420 mF/cm² and very high charging voltage of 6-7 V, but shows very high self discharge and lesser stability compared to CNT-NiO/KOH or graphene-NiO/KOH system.

- We then combined advantages of both systems CNT/NiO and CNT/Ppy by developing an asymmetric battery-type hybrid capacitor in two-electrolyte
system and found that it can store voltage of 4.1-4.3 V even after self discharge with good stability. These studies helped us to develop stable supercapacitors with very high operating voltage.

Integration efforts were then directed by combining the best performing super capacitor, (i.e. CNT/NiO) with DSSC in a single module and found that almost 80% of electrical energy from solar cell is getting stored in supercapacitor. We have developed very high voltage capacity supercapacitors (asymmetric CNT/NiO-CNT/Ppy) which can be integrated with high efficiency solar cell for maximum energy conversion and storage.

The above results helped us to conclude that if the integration scheme can be adequately configured, the integrated device has the potential to replace conventional PV’s and provide a more cost effective system that may reduce dependence on external batteries or other storage systems. Our study showed the elimination of the drawbacks of existing direct energy storage structures to an extent by including independency, so that we can independently optimise the generation and storage sub-components making the integrated concept a plug-and-play system with high flexibility. The super capacitors developed above had different features like high capacitance, high operating voltage and very good stability. Selection of appropriate solar cell and storage units can help us make a solar panel (or tile) which itself inherently stores energy.

This study shows only the preliminary stage of the integration of an energy generating unit with a storage device. To make this as viable technology we need to do more studies for the maximum energy transfer from solar to storage unit and also to reduce self discharge of storage unit after complete charging. Currently some studies are going in this direction, by developing new electronic unit which helps in matching of output load of solar cell to input load of storage unit and also to optimize discharge and load bearing characteristics, hence the stored output can be utilized completely for long time.
Present challenges for introducing robust circuit design to translate solar energy for effective storage include

- Load balancing
- Power loss issues
- Electrical contacts

For load balancing optimizations are going on for the maximum power point tracking (MPPT). Also it is planned develop circuit with lossless sensing (residual loss of only 50 mW per MPPT).

**Future Outlook**

The outstanding challenge for direct solar energy storage is to invent a device incorporating both photovoltaic and storage functions in a single cell structure. Recent study [Neelam Singh1, Charudatta Galande1, Andrea Miranda1, Akshay Mathkar1, Wei Gao2, Arava Leela Mohana Reddy1, Alexandru Vlad1,3 & Pulickel M. Ajayan, printable batteries, SCIENTIFIC REPORTS. 2 : 481, DOI: 10.1038/srep00481] showed a novel approach to battery design from Rice University researchers and they could enable a new type of spray-on batteries by using materials that can be spray-painted onto various surfaces. They integrated a photovoltaic panel with this technology to demonstrate energy capture-storage hybrid devices, which could be integrated into large outdoor surfaces and objects of daily use without constraints of space. Also they found this technique could be used on ceramics, stainless steel, and flexible polymers. If the components of a battery, including electrodes, separator, electrolyte and the current collectors can be designed as paints and applied sequentially to build a complete battery, on any arbitrary surface, it can effect significantly on the design, implementation and integration of energy storage devices. Here, they demonstrated the possibility of interconnected modular spray painted battery units to be coupled to energy conversion devices.

A merit of our developed device is that both generation and storage parts are capable of functioning independently so that photovoltaic unit and storage units can be independently optimized by changing the materials to maximize the performance. The device is capable of repeated photo-charge and discharge. Our study shows an easy method of development of highly capacitive composite
supercapacitor electrodes using cheap raw materials like carbon and polymers but same concept can be extended to independently develop (or enhance existing solar cells) highly efficient and cost-effective solar cells and integrate the PV and storage components seamlessly.

Some of the technical issues faced during the device development are the effective device and packaging level isolation of two systems (PV and storage); prevent leakages of electrolyte (electrolyte of solar cell and electrolyte of supercapacitor system). This aspect is more important considering that direct interaction of electrolytes may degrade the stability of each system.

Prospects for further study include an efficient design and development of an integrated solar cell/storage panel (or tile) with associated electronic circuitry and investigations into effective packaging and circuitry schemes. An interesting area of study could be to maximize solar energy uptake through efficient tracking algorithms and balance the energy units of the PV and storage with minimum losses and maximum peak power delivery over extended periods. Effective packaging and reliability tests of supercapacitors would also be important for baseline standard setting.

A subsequent aspect of the present study is to understand the electrical connection schemes of the supercapacitors/supercapacitor-battery system to get maximum effective capacitance and voltage storage capacity that would be capable of storing solar electrical energy up to 6 to 7 hrs (during day time) and provide effective discharge in a prolonged manner during night time for 7 to 8 hrs. Development of such systems would be very useful for home utility and lighting.