Engineering of Photo-Rechargeable Energy Storage

Ashim Gurung
South Dakota State University

Follow this and additional works at: https://openprairie.sdstate.edu/etd
Part of the Electromagnetics and Photonics Commons, and the Power and Energy Commons

Recommended Citation
https://openprairie.sdstate.edu/etd/2153

This Dissertation - Open Access is brought to you for free and open access by Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange. For more information, please contact michael.biondo@sdstate.edu.
ENGINEERING OF
PHOTO-RECHARGEABLE ENERGY STORAGE

BY
ASHIM GURUNG

A dissertation submitted in partial fulfillment of the requirements for the

Doctor of Philosophy

Major in Electrical Engineering

South Dakota State University

2017
ENGINEERING OF PHOTO-RECHARGEABLE ENERGY STORAGE

This dissertation is approved as a creditable and independent investigation by a candidate for the Doctor of Philosophy in Electrical Engineering degree and is acceptable for meeting the dissertation requirements for this degree. Acceptance of this dissertation does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Qiquan Qiao, Ph.D.  Date
Dissertation Advisor

Steven Hietpas, Ph.D  Date
Head, Department of Electrical Engineering and Computer Science

Dean, Graduate School  Date
I would like to convey sincere gratitude to my dissertation and research advisor Dr. Qiquan Qiao for the opportunity to be a part of his multinational and interdisciplinary research group, Ph.D. program in EECS department and his continual support and motivation towards completion of the degree.

I would also like to express sincere appreciation to Dr. David Galipeau for his time, valuable suggestions, guidance and supervision of my research topic and immaculate correction of my dissertation.

I am grateful to Dr. Reinaldo Tonkoski, Dr. Parashu Kharel, Dr. Huitian Lu and Dr. Jason Zimmerman for their valuable time as committee members with valuable guidance and corrections.

I am also thankful to Dr. Steven Hietpas and to all the staffs of the Department of Electrical Engineering at South Dakota State University for the administrative support during my Ph.D. period.

I would also like to thank my research group members (Khan Mamun Reza, Ke Chen, Rajesh Pathak, Behzad Bahrami, Dr. Hytham Elbohy, Sally Mabrouk, Roya Naderi, Bjorn Vaagensmith, Salem Abdulkarim, Geetha Varnekar, and Dr. Mao Liang) who have helped me for experimental works and suggestions.

Lastly, I would like to thank my family for their invaluable and irreplaceable love and support.
# TABLE OF CONTENTS

**LIST OF FIGURES** .................................................................................................................. vii  
**LIST OF TABLES** .................................................................................................................. xii  
**ABSTRACT** .............................................................................................................................. xiii  

**CHAPTER 1: INTRODUCTION** .................................................................................................. 1  
1.1 Background .......................................................................................................................... 1  
1.2 Previous Work ...................................................................................................................... 9  
1.3 Motivation ........................................................................................................................... 15  
1.4 Objective ............................................................................................................................ 15  

**CHAPTER 2: THEORY** ......................................................................................................... 16  
2.1 Solar cell operation .............................................................................................................. 16  
2.1.1 p-n junction .................................................................................................................... 16  
2.1.2 p-n junction under illumination ...................................................................................... 18  
2.1.3 Working principle of dye sensitized solar cell ................................................................. 20  
2.1.4 Working principle of perovskite solar cell ....................................................................... 23  
2.2 Lithium ion batteries ........................................................................................................... 25  
2.3 Photo-charging of Li-ion Battery ........................................................................................ 27  
2.3.1 Photo-charging of discrete Li-ion battery ....................................................................... 27  
2.3.2 Integrated solar cell/Li-ion battery device ...................................................................... 28  
2.3.3 Boost converter operation .............................................................................................. 30  
2.3.4 Photo electric conversion and storage performance parameters ................................. 31
2.4 Integrated PV/storage cell requirements

CHAPTER 3: PROCEDURES

3.1 Li-ion half and full cells assembly

3.1.1 Slurry formulation

3.1.2 Electrode preparation

3.1.3 Cell assembly and characterization

3.2 Fabrication and characterization of dye sensitized solar cells

3.2.1 Platinum counter electrodes

3.2.2 Photoanode

3.2.3 DSC assembly

3.2.4 Characterization

3.3 Fabrication and characterization of perovskite solar cells

3.3.1 Fabrication of p-i-n perovskite solar cell

3.3.2 Fabrication of n-i-p perovskite solar cell

3.4 Photo charging and discharging of discrete Li-ion battery

3.5 Fabrication and characterization of Li-ion battery on titanium substrate

3.6 Fabrication and characterization of integrated PSC/Ti/Li-ion battery

CHAPTER 4: RESULTS AND ANALYSIS

4.1 Electrochemical charge/discharge performance of TiO_2 and Li_4Ti_5O_12

4.1.1 TiO_2

4.1.2 Li_4Ti_5O_12
4.2 Photo charging of discrete Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ Li-ion battery ........................................... 62

4.2.1 J-V characteristics of DSC and PSC ................................................................. 62

4.2.2 Boost converter operation .................................................................................. 63

4.2.3 Cycling of discrete Li-ion battery using PSC and DSC charging ................. 64

4.2.4. Maximum power operation of photo charging of Li-ion battery ............... 70

4.2.5 Cycling stability of PSC and DSC ...................................................................... 71

4.3 Photovoltaic performance of PSC with transparent top electrode ................. 75

4.3.1 Optical and electrical characteristics of the transparent top electrode .......... 75

4.3.2. I-V performance of PSCs with the semi-transparent top electrode .......... 78

4.3.3. Cycling performance of Li$_4$Ti$_5$O$_{12}$/LiCoO$_2$ Li-ion battery on titanium ... 80

4.5. Photo-charging/discharging of integrated PSC/ Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ Li-ion battery ... 82

4.5.1. Charge/discharge performance of integrated cell ........................................ 82

4.5.2. Maximum power point operation of the integrated cell .............................. 88

4.5.3. Statistics of the photo-charge/dischARGE performance of the integrated cell.. 90

4.5.4 Storage time equivalent of the photo-rechargeable systems ....................... 92

CHAPTER 5: CONCLUSIONS .................................................................................. 96

5.1 Summary ........................................................................................................... 96

5.2 Conclusions ...................................................................................................... 99

5.3 Future Work .................................................................................................... 100

References ............................................................................................................. 101
LIST OF FIGURES

Figure 1.1. Estimated renewable energy share of global electricity production [4]. ........ 3
Figure 1.2. Average annual growth rates of renewable energy (2008-2013) [4]........... 3
Figure 1.3. Solar PV total global capacity trend (2005-2015) [4]. .......................... 4
Figure 1.4. US Electricity Nameplate capacity and generation in 2013 [7]. ............... 4
Figure 1.5. Solar Cell efficiency chart [8]. ................................................................. 5
Figure 1.6. Capacities of different energy storage technologies [33].......................... 7
Figure 1.7. Efficiency and lifetime of storage technologies [33]............................... 7
Figure 1.8. Investment costs of storage devices [33].............................................. 8
Figure 2.1. p-n junction and depletion region [70]..................................................... 17
Figure 2.2. Illuminated p-n junction showing formation of electron-hole pairs [70]..... 19
Figure 2.3. Structure of dye sensitized solar cell -modified from [76]....................... 21
Figure 2.4. Schematic showing operation of dye sensitized solar cell – modified from [75].................................................................................................................. 22
Figure 2.5. Recombination mechanisms and pathways in dye sensitized solar cells. ..... 23
Figure 2.6. p-i-n perovskite solar cell a) device structure b) energy level diagram. ...... 24
Figure 2.7. Schematic showing the operation of Lithium ion battery (full cell). ........... 26
Figure 2.8. Schematic showing the operation of Li-ion half cell.................................. 27
Figure 2.9. Isolated photo charging scheme (a) using perovskite solar cell and (b) dye sensitized solar cell. .............................................................................................. 28
Figure 2.10. Schematic showing operation of perovskite solar cell/Li-ion battery integrated structures with boost converter................................................................. 29
Figure 3.1. Li-ion cells a) half cell and b) full cell. ...................................................... 40
Figure 3.2. Cross-sectional structure of dye sensitized solar cell. ................................. 41
Figure 3.3. Perovskite solar cell device structure (p-i-n structure)............................... 44
Figure 3.4. Perovskite solar cell device structure (n-i-p structure) with semi-transparent  
            top electrode on (a) FTO glass as bottom electrode (b) Ti metal foil as bottom  
            electrode. ........................................................................................................ 46
Figure 3.5. Schematic for (a) photo charging (b) discharging of discrete Li-ion battery. 48
Figure 3.6. Li-ion full cell on Ti substrate ..................................................................... 50
Figure 3.7. Cross sectional view of PSC/Li-ion battery integrated device structure ...... 51
Figure 3.8. Schematic for (a) photo-charging and (b) charging of DSC/Li-ion battery  
            integrated device. ............................................................................................ 52
Figure 4.1. Specific capacity of cathodes P25-TiO$_2$ and anatase-TiO$_2$ half cells........ 54
Figure 4.2. Electrochemical cycling performance of anatase TiO$_2$-LiCoO$_2$ (a) Rate  
            capabilities (b) charge discharge voltage profiles ............................................ 56
Figure 4.3. Efficiencies of anatase TiO$_2$-LiCoO$_2$ full cell (a) energy storage (b)  
            Coulombic ........................................................................................................ 57
Figure 4.4. Electrochemical cycling performance of Li$_4$Ti$_5$O$_{12}$-Li half cell (a) Rate  
            capabilities (b) voltage profiles ....................................................................... 59
Figure 4.5. Electrochemical cycling performance of Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ full cell (a) Rate  
            capabilities (b) voltage profiles ....................................................................... 60
Figure 4.6. Efficiencies of Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ full cell (a) energy storage (b) coulombic. 61
Figure 4.7. J-V characteristics of (a) perovskite solar cell and (b) dye sensitized solar cell. 
                                         ................................................................................................. 62
Figure 4.8. Voltage profiles of Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ cell (a) PSC-charging/discharging: red and black lines 1$^{st}$-10$^{th}$ cycle; dc supply charging/discharging: green and black lines 11$^{th}$-20$^{th}$ cycles; (b) DSC-charging/discharging: blue and black lines 1$^{st}$-10$^{th}$ cycle; dc supply charging/discharging: green and black lines 11$^{th}$-20$^{th}$ cycles.

Figure 4.9. Discharge capacity of Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ cell (a) for PSC-charging (10 cycles) followed by dc supply charging for another 10 cycles; (b) DSC-charging (10 cycles) followed by dc supply charging for another 10 cycles.

Figure 4.10. (a) Energy storage efficiency of PSC-charging; (b) Energy storage efficiency of DSC charging.

Figure 4.11. Photo-charge vs d-supply charge time of the Li-ion cell (a) PSC-charging and (b) DSC-charging.

Figure 4.12. Overall efficiency of the PSC and DSC charging.

Figure 4.13. Coulombic efficiency of the dc supply charging.

Figure 4.14. (a) J-V characteristic curves for different cycles; (b) operating voltage vs cycle number; and (c) PV-battery coupling factor (PV power/P$_{max}$) during the Li$_4$Ti$_5$O$_{12}$/LiCoO$_2$ cell charging.

Figure 4.15. Cycling photovoltaic performance of the solar cells: (a) J-V curve of PSC (b) J-V curve of DSC (c) power conversion efficiency of PSC and DSC over 10 charge/discharge cycles.

Figure 4.16. DMD transparent top electrode. A) thickness of the different layers used; B) Optical transmittance of the top electrode with different layers; AFM.
topography images and 3D-views of (C, D) Ag and (E,F) Au/Ag; G) CS-AFM images of Au/Ag film..............................................................77

Figure 4.17. J-V characteristics of PSCs with Ti (as bottom) and DMD (as top) electrodes versus PSCs with FTO (as bottom) and DMD and Ag (as top) electrodes.. 79

Figure 4.18. (a) specific capacity (b) coulombic efficiency (output charge/input charge) (c) energy storage efficiency (output energy/input energy) of Li$_4$Ti$_5$O$_{12}$/LiCoO$_2$ Li-ion thin film cell versus coin cell. ....................... 81

Figure 4.19. (a) Voltage profiles of Li$_4$Ti$_5$O$_{12}$/LiCoO$_2$ cell: PSC-charging/discharging: red and black lines 1$^{st}$ -5$^{th}$ cycle; DC supply charging/discharging: blue and green lines 6$^{th}$-10$^{th}$ cycles; (b) discharge capacity over number of charge/dischARGE cycles. ..................................................................................... 83

Figure 4.20. Efficiency of PSC/Li$_4$Ti$_5$O$_{12}$/LiCoO$_2$ integrated cell (a) Overall efficiency; (b) Storage efficiency and (c) Coulombic efficiency ....................... 85

Figure 4.21. Rate capability of the PSC/LIB integrated cell. ........................................... 86

Figure 4.22. Cycling photovoltaic performance of the PSC/Li-ion battery integrated cell:
(a) J-V curve (b) average power conversion efficiency over number of charge/dischARGE cycles. ................................................................................. 87

Figure 4.23. (a) J-V characteristic curves for different cycles; (b) operating voltage vs cycle number; and (c) PV-battery coupling factor (PV power/P$_{max}$) during the Li$_4$Ti$_5$O$_{12}$/LiCoO$_2$ cell charging. ................................................................. 90

Figure 4.24. Statistics of (a) overall efficiency and (b) energy storage efficiency of PSC/Li$_4$Ti$_5$O$_{12}$/LiCoO$_2$ integrated cell over three different batches.......... 91
Figure 4.25. (a) Irradiance profile of June 19, 2013; (b) Ramp rate (%/min) indicating number of violations. .......................................................... 92

Figure 4.26. (a) Actual PV power profile and PV power profile satisfying the 10%/min ramp limit; (b) Required battery power and energy to meet the limit. .......... 93

Figure 4.27. Storage time equivalent to meet the different ramp rates...................... 94
LIST OF TABLES

Table 2.1. Seconds of energy storage vs desired ramp rate. ........................................34
Table 3.1. Electrical characteristics of the boost converter ..........................................48
Table 4.1. Photovoltaic performance parameters of solar cells. ....................................63
Table 4.2. Converter operating stages during PSC photo-charging of Li-ion battery ..........63
Table 4.3. Photovoltaic performance parameters of perovskite solar cell for photocharging Li₅Ti₄O₁₂/LiCoO₂ Li-ion battery .................................................................74
Table 4.4. Photovoltaic performance parameters of DSC for photo-charging Li₅Ti₄O₁₂/LiCoO₂ Li-ion battery .................................................................74
Table 4.5. Photovoltaic performance parameters of PSCs with Ti (as bottom) and DMD (as top) electrodes versus PSCs with FTO (as bottom) and DMD (as top) electrodes. ....79
Table 4.6. Photovoltaic performance parameters of PSC/Li-ion battery integrated cell. ..........88
Table 4.7. Storage time equivalent for different ramp rate limits ....................................94
Table 4.8. Summary of the storage time equivalent of the photo rechargeable systems .......95
Solar photovoltaics (PV) is a very promising renewable energy technologies as it is abundant and pollution-free. However, the major drawback of PV power is its intermittency. Integration of batteries with solar modules can reduce overall PV system costs and increase the practicality of PV power. Integration of the photovoltaic cells with supercapacitor storage proved feasibility of combined photovoltaic energy generation and storage but the supercapacitors had low energy storage capacity. Photovoltaic cells with integrated Li-ion batteries as energy storage were demonstrated but had a complex structure due to multiple PV cells; low efficiency due to a mismatch between the PV cell and battery; and low storage capacity due to TiO₂ nanotube structure as battery electrode material which possesses high power density but low energy density. There is a need for an efficient integrated photovoltaic rechargeable energy storage system that is cost effective. The objective of this research was to develop an integrated photovoltaic/energy storage device that uses a single solar cell to simply manufacturing (roll to roll); is more efficient by using MPPT with boost converter; and has higher energy storage using a suitable battery electrode material.

The performance of DSCs, PSCs with a MPPT boost converter using discrete single solar cells to charge batteries were investigated to determine if the MPPT boost converter can provide the boost function with maximum PV power. Integrated PV/energy storage
devices using DSCs, PSCs and Li-ion batteries were fabricated and characterized with MPPT. Li$_4$Ti$_5$O$_{12}$ battery material had greater than 10% higher specific capacity and better cycling stability with 10% higher energy storage efficiency in both half and full cells than TiO$_2$ tested. The efficiency of PSCs were 14.2% vs 7.8% for DSCs. MPPT led to 9% overall efficiency for PSC-charging vs 5% for the DSC. This was attributed to the higher efficiency of PSC. The PSC efficiency decreased by 2.2% while DSC was more stable with a decrease of 0.4% for 10 cycles studied. The overall efficiency was 4.2% for PSC integrated cell. The overall efficiency of the PSC integrated cell was lower than the discrete PSC charging of a Li-ion coin cell. This was attributed to the lower efficiency of the rear illuminated solar cell in the integrated cell. The storage efficiency of the integrated cell was comparable to that of discrete DSC charging of Li-ion coin batteries. A decrease in discharge capacity of the integrated cell was observed similar to that of the thin film battery studied separately. This integrated device had less complex fabrication, higher storage capacity and was more efficient in comparison to previous reports on third generation solar cells such as dye sensitized solar cells. A simple analysis demonstrating the use of the integrated cell for PV ramp rate application showed that the PSC/Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ integrated cell had storage time > 150 secs to satisfy the desired 10%/min ramp rate and also could satisfy even lower ramp rate of 5%/min which required 424 secs. PSCs are at an early development stage and have achieved high efficiency, but stability is a major concern. If this problem is solved then, use of PSC for PV-battery integration will be promising.
CHAPTER 1: INTRODUCTION

1.1 Background

Fossil fuels such as coal, oil and natural gas have been the major sources of electric energy for daily consumption. Use of these fuels leads to production of greenhouse gases which are responsible for global warming, a major topic of global concern. According to International Energy Association (IEA), in 2015, total world fuel supply was 36.1% oil, 18.0% coal and 26.0% natural gas [1]. Therefore, a significant share of energy still comes from traditional fossil fuels. These fossil fuels in addition to being pollution makers are non-renewable. According to the NASA Goddard Institute for Space Studies (GISS), 2016 has already observed record deviation of global earth surface temperature as high as 1.32 °C above 1951-80 average [2, 3]. Therefore, the world community has been in search of alternative energy sources which are renewable and pollution free. According to Renewables 2016 Global Status report [4], by the end of 2015, renewable energy was 23.7% of global electricity production as shown in Figure 1.1. This was distributed to hydropower (16.6%), wind (3.7%), bio-power (2.0%), solar PV (1.2%) and geothermal, CSP and ocean (0.4%).

Solar photovoltaic (PV) is one of the promising renewable energy technologies. Solar energy is abundant and pollution-free. The earth receives about 174 petawatts of solar radiation at the upper atmosphere, out of which 30% is reflected to space and the remaining is absorbed by the Earth’s atmosphere, oceans and land masses [5]. It is estimated that 1 ½ hours of sunlight can meet world’s electricity needs for an entire year [6]. Realization of the potential of this tremendous amount of energy available to the Earth
has pioneered many solar energy applications such as solar heating, cooking and electricity production via photovoltaic (PV) and concentrated solar power (CSP) systems. During the years 2010 through 2015, solar photovoltaics (PV) experienced the fastest capacity growth rate among the renewables as shown in Figure 1.2 [4]. The solar PV global capacity reached 227GW by the end of 2015 as shown in Figure 1.3[4]. Solar PV has contributed an estimated 7.8% of annual electricity demand in Italy, nearly 6.5% in Greece and 6.4% in Germany.

United States has been a forerunner in renewable energy generation. Installed renewable electricity capacity exceeded 179 GW generating 554 TWh as shown in Figure 1.4. Although hydropower and wind accounts for the highest percentage share of the installed capacity and generation, in 2014, solar PV and CSP were the fastest growing renewable electricity technologies which increased by 51.2% (12.1 GW to 18.3GW) and 83.6% (0.91 GW to 1.68 GW) respectively [7]. Solar PV was 48% of US installed renewable electricity in 2014 [7]. Several factors contribute to the growth of solar PV market which includes continuous decline in cost of PV modules, need for green energy and improved solar cell efficiencies.
Figure 1.1. Estimated renewable energy share of global electricity production [4].

Figure 1.2. Average annual growth rates of renewable energy (2008-2013) [4].
**Figure 1.3.** Solar PV total global capacity trend (2005-2015) [4].

**Figure 1.4.** US Electricity Nameplate capacity and generation in 2013 [7].
Production of electricity by conversion of solar energy into electric energy is accomplished by use of solar photovoltaic panels/modules which consist of photovoltaic cells/units (or solar cells) configured in series or parallel. The growth trend in solar cell efficiencies for different technologies is shown in Figure 1.5 [8]. These PV panels are dominantly silicon-based technology with module efficiency of 21.5% [8-11]. Thin film technologies such as copper indium gallium diselenide (CIGS) modules have efficiency of 16.8%. Dye sensitized solar cells have demonstrated efficiency of 11.9% (lab-scale). Perovskite solar cells (PSCs) are the recent vigorously investigated technology and have already achieved a certified cell efficiency of 22.1% reported by KRICT/UNIST [12-30], however, it still has concerns of stability.

Figure 1.5. Chart showing progress in solar cell efficiency (Source: National Renewable Energy Laboratory, 2017).
One of the major drawbacks of PV power is its intermittency as PV power output depends on solar irradiance which is not constant due to clouds and random sun periods [31, 32]. Such power fluctuations are a subject of critical concern in islanded microgrids where grid power is not available for power compensation and in grids where PV power share is high [33, 34]. Electric utilities have imposed power ramp rate limitations for PV grid integration. Compliance with such ramp rate limitation vastly underutilizes PV power availability, so this suggests the use of energy storage.

Several energy storage technologies have been in practice and comparisons of these technologies on basis of power/energy density, efficiency and cost are shown in Figures 1.6, 1.7 and 1.8 respectively [35]. Pumped hydro has been the dominant energy storage technology with the lowest cost and long discharge time. However, special site requirements lead to inflexibility of this technology. Also, compressed air energy storage (CAES) also can store bulk energy and have lower capital cost per unit energy but also has special site requirements. Flywheels and supercapacitors have high power density but low energy density and are expensive. Batteries have high energy density with decent power density but are expensive. Among the battery technologies, lithium ion batteries have revolutionized the electronics industry and thus are being pursued for electric vehicles and grid applications [36-40]. Lithium ion batteries have higher energy density than lead acid and are available in thin film. However, capacity, high cost and safety concern of lithium ion batteries need to be addressed for larger applications.
Figure 1.6. Capacities of different energy storage technologies [35].

Figure 1.7. Efficiency and lifetime of storage technologies [35].
Traditionally, PV energy generation and battery storage is based on PV panels and batteries working as independent units electrically connected via long distance electric wires [41]. Such systems have been used to integrate solar power into the grid. Battery storage is capable of providing multiple functions such as absorbing and delivering both real and reactive power and address ramp rate, frequency and voltage issues related to integration of solar power into grid. However, such systems are bulky, inflexible, require more space, undergo energy loss through external wires and expensive [42]. Integration of batteries with solar modules by combining the two functions: solar PV energy generation and energy storage can potentially reduce overall PV system costs and increase the practicality of PV power. Integrated photovoltaic energy generation and storage cells can be light weight, compact, efficient and have been studied as a cost effective approach.
1.2 Previous Work

Most of the literature reports on integrated solar rechargeable energy storage have been focused on use of solar PV for capacitive energy storage [41, 43-65]. Dye sensitized solar cells has been studied for integration with energy storage devices attributed to its electrochemical compatibility to electrochemical capacitors and batteries. Dye sensitized photo supercapacitors were developed with two electrode and three-electrode designs by Miyaska et al. in 2004 and 2005 respectively. [44]. For the two electrode design, charge voltage of 0.45 V was obtained with discharge capacity of 75 mCcm\(^{-2}\) @ 47 µAcm\(^{-2}\). For the three electrode design, the charge-state voltage reached 0.8 V under 100 mWcm\(^{-2}\) illumination of DSC and galvanostatically discharged (@ 47 µAcm\(^{-2}\)) to 0 V which yielded an energy density of 47 µWhcm\(^{-2}\) with coulombic efficiency of 42% and capacitance of 0.65 Fcm\(^{-2}\). The three electrode design was superior in performance with higher voltage and five times higher energy density. The high internal resistance of the two electrode design retards the discharge process, limiting the performance. No information on solar cell efficiency was provided.

In 2010, H-W. Chen et al., developed a flexible photo-rechargeable capacitor using a three electrode configuration separating a flexible dye sensitized solar cell and a PEDOT-based supercapacitor by sharing a common Pt electrode [45]. The photocapacitor was charged in 900 s under 100 mWcm\(^{-2}\) of a plastic DSC (4.37% efficiency) to 0.69 V and galvanostatically discharged to 0 V in 150 s @ 2 mAcm\(^{-2}\) which obtained a capacitance of 0.52 Fcm\(^{-2}\). This corresponded to time equivalent of 27 s (the calculation of this time equivalent has been explained in section 2.4) of maximum PV power (\(P_{\text{max}}\)) energy storage
which is less than the reserve energy capacity of 243 s to meet the ramp rate requirement as described in Section 2.4.

An all-solid state integrated device was developed using free standing and aligned multi-walled carbon nanotube (MWCNT) films as electrodes by Z. Yang et al. in 2013 [41]. The device was charged to 0.72 V in 8 s under 100 mW 1.5 AM illumination of a 6.1% efficient DSC and galvanostatically discharged to 0 V in 35 s which had a coulombic efficiency of 84% and overall efficiency of 5.12%. The integrated device which incorporated polyaniline into MWCNT film was charged in 33 s and galvanostatically discharged to 0 V in 144 s with a coulombic efficiency of 70% and overall efficiency of 4.29%. Also, a flexible integrated device was fabricated which showed a charging time of 183 s, discharge time of 137 s @ 1.4 mAcm$^{-2}$, a specific capacitance of 83 Fg$^{-1}$, coulombic efficiency of 34% and overall efficiency of 0.79%. This corresponded to time equivalent of 33 s of $P_{\text{max}}$ energy storage which is less than the reserve energy capacity of 243 s.

In 2015, an all silicon electrode photocapacitor was demonstrated for integrated energy storage and conversion by A. Cohn et al. Porous silicon was used as a common electrode acting as counter electrode of dye sensitized solar cell and supercapacitor electrode. The integrated device could be charged to 0.64 V and achieved an energy density of 0.17 µWhcm$^{-2}$ and capacitance of 3.5 mFcm$^{-2}$ with an overall efficiency of 2.1 %. The energy storage corresponded to time equivalent of 0.12 s which is much lower than 243 s.

Two-electrode integrated device was realized by fabrication of a more complex photovoltaically self-charging cell by modifying the counter electrode of a dye sensitized solar cell with Pt/Au/PVDF/ZnO nanowire composite (Zhang et al., 2013) [66]. This device
had the high dielectric constant of PVDF and high surface area of nanomaterial with reported solar cell efficiency 3.7%, stored charge density of 2.14 Cg$^{-1}$ and stored energy density of 1.4 mWhkg$^{-1}$. No discharge current was provided to calculate the energy storage. However, the stored energy density was lower than reported results of typical supercapacitors.

In 2014, coaxial integration of dye sensitized solar cell and electrochemical capacitor into a fiber structure was reported with specific capacitance of 3.32 mFcm$^{-2}$. The device was charged to 0.63 V and discharged with overall efficiency of 2.73% and energy storage efficiency of 75.7%. The energy storage corresponded to time equivalent of 2.5 s which is much lower than 243 s.

The integrated solar cell-supercapacitor devices were only able to store a limited amount of energy because supercapacitors have low energy density and the cost ($/kWh) is higher for supercapacitors [35]. Batteries have higher energy density and $/kWh is lower compared to supercapacitors [35].

Batteries have been studied for integration with solar cells. Use of a single junction silicon solar cell integrated with silicon nanowire/ lithium ion battery on a common Si substrate was investigated by Kohl and co-workers in 2012 [67]. They studied the effect of Li$^+$ ion back diffusion into the solar cell from the Si battery anode. Li is a fast diffuser in Si with a room temperature diffusivity of $2 \times 10^{-10}$ cm$^2$s$^{-1}$ which can lead to Si amorphousization and degradation of PV performance. With no barrier layer, a well-defined lithiation peak followed by no delithiation peak was observed indicating that Li$^+$ diffused into the PV cell and not available during delithiation. However, use of TiN as
barrier layer, well-defined lithiation followed by delithiation peaks were observed indicating that barrier layer could efficiently block Li$^+$ diffusion. However, no study of illumination of the solar cell for storage was performed. In addition, the silicon solar cells required expensive deposition systems with requirement of high purity material. Also, silicon when used as battery anode suffered from a large volume change during lithiation resulting in poor cycling.

Ye et al. reported an integrated rechargeable thin film Nb$_2$O$_5$/LiPON/LiMn$_2$O$_4$ battery on a purchased amorphous silicon thin film solar cell with 5 series units. The solar cell had an efficiency of 7.4%. The thin film battery electrodes and electrolyte were deposited using RF-magnetron sputtering. Upon solar charging, the composite device exhibited a low discharge capacity of 215 µAh for 10 min charging time. The energy stored was 2.4 s which is much lower than 243 s.

Recently, Um et al. demonstrated a monolithically integrated design consisting of crystalline silicon solar cells and lithium ion battery. This design used aluminum metal electrode of the PV module as the current collector for the LIB [68]. The integrated power pack consisted of 25 units of Si solar cells connected in series and a solid state LIB with a bipolar cell configuration fabricated using an ultraviolet curing-assisted printing process. The highest photo-electric conversion/storage efficiency reported so far of 7.61% was reported using a 15.8% efficient c-Si solar module. The integrated cell could be discharged in 16 mins at a rate of 0.5 mAcm$^{-2}$. This was equivalent to 142 s which is lower than the required 243 s.
Other thin-film solar cell technologies such as CIGS offer flexible and roll to roll manufacturing, but no reports of use of CIGS solar cells for integration with battery have been reported. CIGS solar cells suffer from disadvantages such as materials unavailability and toxicity issues.

Dye sensitized solar cells have been considered a promising low cost solar cell technology because they can be solution processed and easily made [69-71]. A dye sensitized solar cell was integrated with a lithium-air battery by M. Yu et al. in 2014 [72]. The objective was to decrease charging voltage to match discharging voltage of the lithium air battery. The photo charging led to decrease in charging over potential from 3.8 V to 3.4 V. The integrated device still required an external charging source to fully charge the battery. In addition, instability of charging voltage was observed and was stable only up to 3 cycles. Similar work was reported with integration of dye sensitized photoelectrode in a LiI redox flow battery via linkage of I\textsuperscript{3}/I\textsuperscript{-} based catholyte which led to reduction of charging voltage from 3.6 V to 2.9 V [73]. However, these devices still required an external charging source to fully charge the battery. Recently, dye sensitized electrode integrated into a redox battery has been reported with a discharge capacity of 240 µAhcm\textsuperscript{-2} with storage efficiency of 78% [74]. The energy stored was 355 s which is higher than the required 243 s. However, the solar cell efficiency was only 1.7%. Overall efficiency was not mentioned and the device operation was complex.

Lately, Perovskite solar cell (PSCs) has been considered as a breakthrough technology to achieve cost objectives. These cells can be solution processed and are low cost [75]. The use of PSCs has been investigated for battery charging. Recently, in 2015, four series connected PSCs were employed to charge a LiFePO\textsubscript{4}/Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} LIB [76]. The
series connected PSCs provided the required charging voltage with $V_{oc}$ of 3.84 V and efficiency of 12.65%. The overall system efficiency of 7.8% at 0.1 C and 7.36% at 0.5 C was achieved with a storage efficiency of ~60%. However, the solar cell and battery were not integrated and no maximum power tracking was employed.

A tandem dye sensitized solar cells with thin film Li ion battery integrated device was developed by Guo et al. in 2012 [42]. The integrated pack consisted of TiO$_2$ NTs grown on both sides of Ti foil. The solar cell consisted of TiO$_2$ nanorods sensitized by N719 dye as top cell and TiO$_2$ nanotubes sensitized by N749 dye as bottom cell. The integrated battery was charged from 550 mV to 2996 mV in 440 s. At a discharge current of 100 μA, the device showed a capacity of only 33.89 μAh. The energy stored was equivalent to 125 s which is less than 243s. The overall system efficiency was only ~0.82% with energy storage efficiency of 41%. The tandem solar cell made device fabrication complicated and no maximum power tracking was used.

Recently, a two-electrode solar rechargeable LIB was demonstrated by Zaghib et al. that worked on direct photo-oxidation of lithium iron phosphate (LiFePO$_4$) nanocrystals in presence of dye as hybrid cathode and lithium metal as anode [77]. Dye generated holes led to delithiation of LiFePO$_4$ to form FePO$_4$ and electrons led to reduction of oxygen forming peroxides. These oxygen products reacted with carbonate based electrolyte to form solid electrolyte interphase layer like in a lithium air battery. However, the overall efficiency of the system was only 0.06-0.08%.

In summary, integration of the photovoltaic cells with supercapacitor storage proved feasibility of combined photovoltaic energy generation and storage but the
supercapacitors had low energy storage capacity. Photovoltaic cells with integrated Li-ion batteries as energy storage were demonstrated but had a complex structure due to multiple PV cells; low efficiency due to a mismatch between the PV cell and battery; and low storage capacity due to TiO$_2$ nanotube structure as battery electrode material which possesses high power density but low energy density.

1.3 Motivation

There is a need for an efficient integrated photovoltaic rechargeable energy storage system that is cost effective.

1.4 Objective

The goal of this research was to develop an integrated photovoltaic/energy storage device that uses a single solar cell to simplify manufacturing (roll to roll); is more efficient by using MPPT with boost converter; and has higher energy storage using a suitable battery electrode material.
CHAPTER 2: THEORY

2.1 Solar cell operation

A solar cell absorbs solar energy and converts into electric energy as output. Structurally the simplest form of solar cell is a p-n junction.

2.1.1 p-n junction

Intrinsic silicon is not conductive and therefore is doped with materials such as phosphorous to make it an electron donor (which is n-type) and boron to make it an electron acceptor (which is p-type). A solar cell consists of two doped semiconductor materials (one p-type and another n-type) brought in physical contact with each other. Therefore, it is also commonly referred to as a p-n junction.

A concentration gradient exists for both electrons and holes when n-type and p-type silicon materials are brought in contact. This concentration gradient causes diffusion of electrons into the p-side and holes into the n-side of the junction. Diffusion current density for electrons, $J_{n,\text{diff}}$, and holes, $J_{p,\text{diff}}$, are described by [78]:

$$J_{n,\text{diff}} = qD_n \frac{dn(x)}{dx}, J_{p,\text{diff}} = -qD_p \frac{dp(x)}{dx} \tag{2.1}$$

where, $q$ is the electron charge, $D_n$ and $D_p$ are the diffusion coefficients for electrons and holes, $n$ and $p$ are the electron and hole concentrations.

Figure 2.1 shows p-n junction and depletion region. The diffused electrons enter the p-side and recombine with holes near the junction and simultaneously diffused holes enter the n-side and recombine with electrons near the junction. Therefore, the concentration of free charge carriers becomes very low at the region near the junction compared to region
far away from the junction [79]. Therefore, the region near the junction is depleted of free charge carriers and is referred to as the depletion region. Electrons leaving n-side leave behind positively charged ions and holes leaving p-side leave behind negatively charged ions in the depletion region. An internal electric field is developed that is directed from positive ions towards negative ions. This electric field counteracts the diffusion by drifting holes towards the p-side and electrons towards the n-side. Drift current density for electrons ($J_n$) and holes ($J_p$) are [80]:

$$J_n = qn \mu_n E, \quad J_p = qp \mu_p E$$ (2.2)

where, $\mu_n$ and $\mu_p$ are the mobilities of electrons and holes, and $E$ is the applied electric field intensity. This process continues until equilibrium is reached.

**Figure 2.1.** p-n junction and depletion region [79].
2.1.2 p-n junction under illumination

Figure 2.2 shows an illuminated p-n junction with the generation of electron-hole pairs. A material absorbs solar photons when the energy of the photon exceeds the band gap of that material where energy of a photon \( E \) is [81]

\[
E = h\nu = \frac{hc}{\lambda} \quad \text{(in joules)} = \frac{1.24}{\lambda} \quad \text{(in eV)}
\]  

(2.3)

where, \( h \) is the Planck’s constant \( (6.63 \times 10^{-34} \text{ J-s}) \), \( \nu \) is the frequency of photon in Hertz, \( c \) is the speed of light \( (2.998 \times 10^8 \text{ m/s}) \) and \( \lambda \) is the wavelength of the photon in meters.

Band gap is the energy level difference between valence band and conduction band. The absorption of this photon results in electron excitement from the valence band to conduction band which means an electron-hole pair (EHP) is generated [79, 82]. If an EHP is formed within the junction, the built in electric field sweeps electrons towards the n-side and holes towards p-side. These free charge carriers become excess majority carriers (electrons in the n-side and holes in the p-side). These excess majority charge carriers produce current in an external circuit. Likewise, if an EHP is formed in either n-side or p-side, the minority carrier (electron in p-side and hole in n-side) needs to reach the junction to be able to contribute to device conduction current [82]. The time that the minority carrier takes to reach the junction is called minority carrier lifetime, \( \tau_m \), and the maximum distance it can travel before it recombines is called minority carrier diffusion length, \( L_m \), which is expressed as:

\[
L_m = \sqrt{D_m \tau_m}
\]  

(2.4)

where, \( D_m \) is the diffusion constant and \( m \) is the electrons or holes.
Generation of excess charge carriers leads to current flow when two terminals of the device are shorted. This is called photocurrent \( (I_{ph}) \) or short circuit current \( (I_{sc}) \) which is proportional to the intensity of incident solar radiation \( (I) \). When the device is connected to an external load, a voltage appears across the junction which creates current flowing in opposite direction to \( I_{ph} \) [81]. This current is called forward diode current \( (I_d) \) expressed as [81]:

\[
I_d = I_o \left[ \exp \left( \frac{eV}{\eta kT} \right) - 1 \right]
\]  

(2.5)

where, \( I_o \) is the reverse saturation current, \( \eta \) is the ideality factor (ranges from 1 to 2), \( e \) is the elementary charge, \( k \) is the Boltzmann constant and \( T \) is the temperature in Kelvin.

The net current flow in a solar cell is therefore:
\[ I = I_d - I_{ph} = I_o \left[ \exp \left( \frac{eV}{\eta k T} \right) - 1 \right] - I_{sc} \]  \hspace{1cm} (2.6)

The open circuit voltage, \( V_{oc} \), can be obtained when \( I \) is set to zero as:

\[ V_{oc} = \frac{kT}{e} \ln \left( \frac{I_{sc} I_o}{I_o + 1} \right) \]  \hspace{1cm} (2.7)

Other performance parameters that define a solar cell are fill factor (FF) and efficiency (\( \eta \)). FF measures the closeness of the real I-V curve to the ideal rectangular shape and is expressed as [82]:

\[ FF = \frac{I_m V_m}{I_{sc} V_{oc}} \]  \hspace{1cm} (2.8)

where, \( I_m \) is the current at maximum power point and \( V_m \) is the voltage at maximum power point. Efficiency is the ratio of output electrical power density to input power density, \( P_{in} \), defined as [81]:

\[ \eta = \frac{P_m}{P_{in}} = \frac{I_{sc} V_{oc} FF}{P_{in}}. \]  \hspace{1cm} (2.9)

2.1.3 Working principle of dye sensitized solar cell

Dye sensitized solar cells (DSC) offer advantages such as low cost, ease of fabrication and reasonable conversion efficiency. Figure 2.3 shows the structure of a dye sensitized solar cell. It consists of electron acceptor usually a mesoporous titanium dioxide (TiO\(_2\)) layer sensitized by light absorber (dye) on fluorine doped tin oxide (FTO) glass as the photoanode, and catalytic metal usually platinum on FTO glass as the counter electrode.
separated by an liquid electrolyte containing iodide/tri-iodide redox couple as a mediator for dye regeneration [83, 84].

Figure 2.3. Structure of dye sensitized solar cell -modified from [85].

Figure 2.4 shows a schematic of the operation of a dye sensitized solar cell. Upon exposure to light, incoming photons are absorbed by the dye which results in excitation of an electron from the ground state(S) of the dye to the excited state(S*) [86].

\[
TiO_2|S + h\vartheta \rightarrow TiO_2|S^*. \tag{2.10}
\]

where, \( h \) is Planck’s constant, \( \vartheta \) is photon frequency, \( h\vartheta \) is photon energy. The electron in excited state is injected into the conduction band of TiO\(_2\) oxidizing the dye molecule (S\(^+\)). This process occurs in order of femtoseconds as

\[
TiO_2|S^* \rightarrow TiO_2|S^+ + e^- \tag{2.11}
\]

Injected electrons travel in TiO\(_2\) primarily by diffusion and get collected at transparent conducting oxide glass (TCO-commonly used fluorine doped tin oxide). The electron helps
to reduce tri-iodide in the electrolyte to produce iodide. Platinum acts as a catalyst to perform the tri-iodide reduction process as

$$I_3^- + 2e^- \rightarrow 3I^-.$$  \hspace{1cm} (2.12)

Iodide ions reduce the oxidized dye by donating an electron and this process regenerates the dye as

$$TiO_2|2S^+ + 3I^- \rightarrow TiO_2|2S + I_3^-.$$  \hspace{1cm} (2.13)

**Figure 2.4.** Schematic showing operation of dye sensitized solar cell – modified from [84]

Figure 2.5 shows the recombination mechanisms and pathways in dye sensitized solar cells that occur which reduce device current [86, 87]. Electrons in excited state of dye can fall back to ground state of dye via process known as photoluminescence which emits photons. Injected electron into the conduction band of TiO$_2$ can recombine with oxidized dye molecule. This process takes place in order of milliseconds. Trap states in TiO$_2$ act as
recombination centers and hinder charge transport process in TiO$_2$. Also, injected electrons in the conduction band of TiO$_2$ can recombine via reduction of tri-iodide to form iodide at the TiO$_2$/electrolyte interface.

![Diagram of recombination mechanisms and pathways in dye sensitized solar cells.](image)

**Figure 2.5.** Recombination mechanisms and pathways in dye sensitized solar cells.

2.1.4 Working principle of perovskite solar cell

Figure 2.6a) shows the pin structure of perovskite solar cell. In pin perovskite solar cell, the hole transport layer is at the bottom with the substrate and the electron transport layer is at the top with the metal contact. Figure 2.6b) shows the corresponding energy level diagram of the structure. The perovskite is the light absorbing layer. Photon absorption by the perovskite layer results in formation of an electron hole pair. The electron and hole separation occurs at the interface between electron transport layer/perovskite and hole transport layer/perovskite. These separated electrons and holes are transferred to the
electron and hole transport layers where they get transported to the respective charge collecting contacts [13-15].

Figure 2.6. p-i-n perovskite solar cell a) device structure b) energy level diagram.
2.2 Lithium ion batteries

Li-ion batteries are electrochemical devices that can store energy. A typical Li-ion battery is composed of two electrodes: anode (+) and cathode (-) electrically isolated by a polymer membrane called separator and ionically connected by an electrolyte. The anode commonly is graphite on copper substrate and cathode is lithium cobalt oxide (LiCoO$_2$) on aluminum substrate [37, 88]. A separator that is commonly used is porous polyethylene and the electrolyte is commonly a lithium salt (e.g. LiPF$_6$) dissolved in organic solvent EC:DMC:DEC (1:1:1 volume ratio).

Figure 2.7 shows a schematic of the operation of a Li-ion battery. During charging (supplying energy from an external dc source), Li ions are de-intercalated from cathode structure and move via electrolyte towards anode structure where they intercalate [89]. For conservation of charge, electrons move out of the cathode towards anode via the external circuit. The electrolyte facilitates the movement of ions. The separator provides electrical isolation but allows Li-ions to pass through its porous structure. Similarly, during discharging (delivering energy to an external load), Li ions de-intercalate from the anode structure and move via electrolyte towards cathode structure where they intercalate. To satisfy conservation of charge, electrons move from anode to cathode via the external circuit. The electrolyte and separator perform the same functions as in the case of charging. Therefore, during full cell charging, anode (e.g. Li$_4$Ti$_5$O$_{12}$ in this case) is reduced and cathode (e.g. LiCoO$_2$) is oxidized as:

Charging:

\[
\text{reduction: } \quad xe^- + xLi^+ + Li_4Ti_5O_{12} \rightarrow Li_{4+x}Ti_5O_{12} \tag{2.14}
\]
Figure 2.7. Schematic showing the operation of Lithium ion battery (full cell).

Figure 2.8 shows a schematic of the operation of Li-ion half cell. Half cells are used to characterize either potential anode or cathode materials where, lithium metal is used as counter or reference electrode, and the material under test is used as working electrode. In half cell charging, lithium is reduced and working electrode (e.g. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in this case) is oxidized. The reverse reaction takes place during discharging as:

Charging:

\[
\text{reduction: } xe^- + x\text{Li}^+ \rightarrow x\text{Li} \tag{2.16}
\]

oxidation: $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12} \rightarrow \text{Li}_4\text{Ti}_5\text{O}_{12} + x\text{Li}^+ + xe^- \tag{2.17}$
2.3 Photo-charging of Li-ion Battery

2.3.1 Photo-charging of discrete Li-ion battery

Figure 2.9 shows the photo-charging scheme of a discrete lithium ion battery using (a) perovskite solar cell and (b) dye sensitized solar cell. The solar cell provides the function of a dc charging source. The output voltage of the solar cell is not high enough to charge the battery. Therefore, a DC-DC boost converter is used to step up the low voltage at the solar cell to a higher voltage required to charge the lithium ion battery. During charging, the Li$^+$ ion and electron move from cathode to anode via the electrolyte and external circuit respectively as previously described.
Figure 2.9. Isolated photo charging scheme (a) using perovskite solar cell and (b) dye sensitized solar cell.

2.3.2 Integrated solar cell/Li-ion battery device

Figure 2.10 shows an integrated perovskite solar cell/Lithium ion battery which consists of the perovskite solar cell on top and the Li-ion battery on bottom with a shared
titanium substrate common electrode and a boost converter to match the PV voltage to the battery voltage. For this integrated structure, the perovskite solar cell requires rear-illumination which means the sunlight has to be incident from the top electrode side. Upon illumination, the positive charges from PV top electrode go to boost converter which steps up the voltage. Positive charges travel to battery cathode and negative charges flow from common electrode. The requirements for the integrated cell include suitable boost converter, transparent top electrode for PV cell, battery anode compatible with common substrate and thin film Li-ion battery. PSCs have higher efficiency and voltage than DSCs but are less stable. [90]

**Figure 2.10.** Schematic showing operation of perovskite solar cell/Li-ion battery integrated structures with boost converter.
Discharging occurs via a load connected across the Li-ion battery. During discharging, the same process takes place as in the case of a typical stand-alone Li-ion battery.

2.3.3 Boost converter operation

The boost converter (bq25504 family) is an ultra low power charger with battery management designed to efficiently harvest microwatts to milliwatts of power generated from DC sources such as photovoltaic. The boost converter functions as a battery charger that requires only microwatts of power to begin operating. A minimum voltage of 330 mV is required for initial startup of the converter. The primary function of the boost converter (Figure 2.10) is to step-up the dc voltage output of the solar cell to the required battery charging voltage level. The converter has two operating stages: (1) cold startup and (2) main boost charging. The cold startup is the inefficient operating mode of the converter where output of the converter is less than the threshold voltage of 1.8 V provided that the input power > 15 µW and Vin > 330 mV. After the output of the converter reaches 1.8 V, the main boost charging mode begins. This main boost charging is the efficient operating mode of the converter. This mode employs pulse frequency modulation mode of control to regulate the voltage at Vin close to the desired reference voltage. The reference voltage is set by the MPPT control. This charging continues until the charge cut-off voltage of 3.14 V. The converter also performs MPPT tracking where it periodically samples the open circuit voltage of the solar cell every 16 seconds by disabling boost function for 256 ms [91]. Boost becomes active at 78% of the open circuit voltage. The MPPT becomes active when the output voltage of the converter and battery is 2.0 V. The battery charging current (output of the converter) is considered constant as the solar cell is illuminated with a constant light illumination. However, in real practice, the battery charging current is
expected to decrease with the increase in the state of charge of the battery as battery resistance increases with charging. The battery is considered fully charged when the charged battery reached the cut off voltage of 3.14 V and this is followed by discharge with cut off voltage of 1 V.

The conversion efficiency of the converter ($\eta_{\text{converter}}$) is defined as:

$$\eta_{\text{converter}} = \frac{\text{battery charging power}}{\text{measured PV power}} \times 100\% \quad (2.18)$$

Coupling factor defines how close to the PV maximum power point the battery charging actually occurs.

$$\text{Coupling factor} = \frac{\text{measured PV power}}{\text{maximum PV power}} \times 100\% \quad (2.19)$$

2.3.4 Photo electric conversion and storage performance parameters

The performance parameters that define the photo electric energy conversion and storage of the photo-charging of Li-ion battery storage are as follows.

The fill factor (FF) of the solar cell is defined as the ratio of the maximum power to the product of open circuit voltage and short-circuit current. It is a measure of squareness of the IV curve of the solar cell and is defined as:

$$FF = \frac{P_{\text{max}}}{I_{sc}} \times V_{oc} \quad (2.20)$$

where, $P_{\text{max}}$, $I_{sc}$ and $V_{oc}$ are maximum power, short-circuit current and open-circuit voltage respectively.
The photo conversion efficiency of the solar cell ($\eta_{solar}$) measures the output power of the solar cell for a given input light energy and is defined as:

$$\eta_{solar} = \frac{(J_{sc} \times V_{oc} \times FF)}{P_{in}} \times 100\% \quad (2.21)$$

where, $J_{sc}$ and $P_{in}$ are short-circuit current density and incident light power density (100 mWcm$^{-2}$) respectively.

The overall photo-electric energy conversion and storage efficiency ($\eta_{overall}$) measures the output (discharge) energy of the storage for a given input light energy and is defined as [76]:

$$\eta_{overall} = \frac{E_{discharge}}{(P_{in} \times A \times t_{ch})} \times 100\% \quad (2.22)$$

where, $E_{discharge}$ is the discharge energy of Li-ion battery, $A$ is the solar cell area and $t_{ch}$ is the photo-charging time.

The storage efficiency ($\eta_{storage}$) measures the output (discharge) energy of the battery to the input (charge) energy.

For photo-charging, $\eta_{storage}$ is defined as [76, 92]:

$$\eta_{storage} = \frac{\eta_{overall}}{\eta_{solar} \times \eta_{converter}} \times 100\% \quad (2.23)$$

For dc supply-charging $\eta_{storage}$ is defined as:

$$\eta_{storage} = \frac{E_{discharge}}{E_{charge}} \times 100\% \quad (2.24)$$

where, $E_{charge}$ is the energy required to charge Li-ion battery.
The coulombic efficiency of Li-ion battery ($\eta_{CE}$) measures the output (discharge) capacity to the input (charge) capacity and is defined as:

$$\eta_{CE} = \frac{C_{\text{discharge}}}{C_{\text{charge}}} \times 100\% \quad (2.25)$$

where, $C_{\text{discharge}}$ and $C_{\text{charge}}$ are the discharge and charge capacities of Li-ion battery.

2.4 Integrated PV/storage cell requirements

The only PV utility reference found that discussed ramp rate requirements was by the Puerto Rico Electric Power Authority (PREPA). Puerto Rico is an islanded grid with a high penetration of renewables. They have set a 10% per minute maximum ramp rate requirement on PV plants connected to the grid [33]. Figure 2.11 shows % power vs time for a ramp rate of 10%/min which for this work was considered a worst case. The reserve energy capacity required ($E$) to ramp down from a 90%/s step change (typical of PV cells in passing clouds) [93] to 10%/min per watt is the shaded area in Figure 2.11 and can be calculated using:

$$E = \frac{1}{2} \times P_{\text{dec}} \times t \quad (2.26)$$

where, $P_{\text{dec}}$ is % power decrease and $t$ is the time to go from 100% to 10% power. For a 1 W PV cell, $P_{\text{dec}}$ would be 0.9 W for 90%, for $t$ of 9 mins, the required reserved energy capacity would be 67.5 mWh/W, which is equivalent to 0.0675 h or 243 s since W in the numerator and denominator cancel out. The seconds of energy storage for this and several other ramp rates are shown in Table 2.1.
For a hydro-PV electric system with a mechanical governor [93], the maximum ramp rate that allowed the system frequency to stay within $\pm 2\%$ limit was 3%/s, which is equivalent to 12.5 s of energy/W. However, if an electronically controlled dump load is added to the hydro-PV system, no extra storage is needed to meet a 90%/s step change.

**Table 2.1.** Seconds of energy storage vs desired ramp rate.

<table>
<thead>
<tr>
<th>Desired ramp rate (%/min)</th>
<th>Seconds of energy storage (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>243</td>
</tr>
<tr>
<td>20</td>
<td>121</td>
</tr>
<tr>
<td>50</td>
<td>48</td>
</tr>
<tr>
<td>90</td>
<td>27</td>
</tr>
<tr>
<td>100</td>
<td>24</td>
</tr>
<tr>
<td>150</td>
<td>16</td>
</tr>
<tr>
<td>200</td>
<td>12</td>
</tr>
</tbody>
</table>

In order to determine the seconds of energy storage at the PV rated power of an integrated cell, the peak rated PV power ($P_{max}$) can be found from the cell efficiency $\eta$ and area $A$ using

$$P_{max} = \eta \times A \times 100 \text{ mW cm}^{-2}$$  \hspace{1cm} (2.27)

where, 100 mWcm$^2$ is illumination intensity. The power density ($P$) is:

$$P = \frac{P_{max}}{A}$$  \hspace{1cm} (2.28)
and the energy storage density \( (E_{\text{storage}}) \) is:

\[
E_{\text{storage}} = J \times V \times t \tag{2.29}
\]

where, \( J \) is the current density, \( V \) is the average discharge voltage and \( t \) is the total discharge time. Then, the time equivalent of the storage capacity \( (T_{\text{storage}}) \) is:

\[
T_{\text{storage}} = \frac{E_{\text{storage}}}{P} \tag{2.30}
\]

For the integrated DSC/supercapacitor in ref [45], the DSC efficiency was 4.37% and the area was 0.25 cm\(^2\). Therefore, the \( P_{\text{max}} \) was 1.0925 mW and \( P \) was 4.37 mWcm\(^2\).

For a \( J \) of 2 mAcm\(^{-2}\), \( V \) of 0.4 V and \( t \) of 150s, \( E_{\text{storage}} \) was 0.0333 mWhcm\(^2\) which yielded a time equivalent \( T_{\text{storage}} \) of 27 s. This time equivalent is less than the reserve capacity of 243 s. According to Table 2.1, this cell could meet a 90%/min ramp rate.

Similarly, for the integrated tandem DSC/lithium ion battery in ref [42], the solar cell power density was 1.95 mWcm\(^2\). The integrated device had discharge capacity of 33.89 µAh with average discharge voltage of 2 V. Assuming area of 1 cm\(^2\) of the battery, \( E_{\text{storage}} \) was 0.068 mWhcm\(^2\). This yielded a time equivalent, \( T_{\text{storage}} \) of 125s which is higher than the supercapacitor storage but lower than the desired value of 243 s to meet a 10%/min ramp rate requirement. According to table 2.1, it could meet 20%/min ramp rate.

For an integrated DSC/lithium ion battery studied in this work, the rear illumination efficiency of DSC is expected to be around 3% with area of 0.33 cm\(^2\) which yields a \( P_{\text{max}} \) of 0.99 mW and \( P \) of 3 mWcm\(^2\). For a typical Li\(_4\)Ti\(_5\)O\(_12\)-LiCoO\(_2\) Li ion coin battery fabricated for this work (electrode area of 1.26 cm\(^2\)), the discharge energy would be about 1 mWh resulting in \( E_{\text{storage}} \) of 0.793 mWh/cm\(^2\) and a time equivalent, \( T_{\text{storage}} \) of 951 s which
is higher than the required reserve of 243 s to meet the 10% ramp rate. The typical Li-ion coin cell battery thickness, excluding battery cases was 0.2 mm. In thin film form, the typical battery thickness would be about the same, and would also be similar to the thickness of a DSC or PSC cell.

**Figure 2.11.** % of power vs time for ramp rate of 10%/min.
CHAPTER 3: PROCEDURES

The tasks to achieve the objective were:

1. Investigate battery anode materials compatible with common electrode substrate (titanium) such as titanium dioxide (TiO$_2$), lithium titanate (Li$_4$Ti$_5$O$_{12}$).

2. Investigate performance of DSCs, PSCs and MPPT boost converter using solar cells to charge batteries.

3. Investigate the photo charging of a Li-ion battery (Li$_4$Ti$_5$O$_{12}$/LiCoO$_2$) using DSCs and PSCs.

4. Investigate suitable transparent top electrode for efficient back illumination of perovskite solar cell/Li-ion battery integrated cell.

5. Fabricate and characterize thin film flexible Li-ion battery on common electrode substrate.

6. Fabricate and characterize integrated PV/energy storage device using PSC and thin film Li-ion battery.
3.1 Li-ion half and full cells assembly

The battery anode materials tested were titanium dioxide ($\text{TiO}_2$) and lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$).

3.1.1 Slurry formulation

For the preparation of slurry, 6 wt% of Polyvinylidene fluoride (PVDF) used as a binder material was dissolved in N-methyl-2-pyrrolidone (NMP) solvent. Active materials ($\text{TiO}_2$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) were mixed with super P carbon black used as conductive additive in weight ratio of 80:10 which was followed by mixing with the PVDF/NMP solution. PVDF was 10 wt% in the mixture. Suitable amount of NMP was further added into the slurry to make the slurry viscous. The slurry was magnetically stirred overnight.

3.1.2 Electrode preparation

A copper (Cu) metal foil was spread on to a glass surface. Acetone was used underneath the Cu foil to ensure that there were no air bubbles between the foil and the glass. Using two layers of masking tape, the region to be coated was defined. The slurry was doctor bladed on to the Cu foil. The coating was dried in vacuum at 100 °C for 12 h. The coating was punched into circular discs of 12.7 mm diameter as battery electrodes and weighed.

3.1.3 Cell assembly and characterization

The prepared electrodes were used in half cell and full cell configurations as shown in Figure 3.1. Half cells (Figure 3.1a) were constructed to study the capacity of $\text{TiO}_2$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with respect to lithium in order to determine the operating voltages and specific
capacity of individual material. In half cell, lithium metal was used as counter electrode or anode and the electrode under test as working electrode or cathode. CR2032 coin cells were used. The working electrode coated on Cu foil with TiO$_2$ or Li$_4$Ti$_5$O$_{12}$ as the active material was placed on top of the positive cell case and positioned at the center of the case. 15 drops of the liquid electrolyte using 1 ml syringe was dropped on top of the working electrode. Polyethylene Celgard separator was placed on top of the electrolyte. Then, 15 drops of the liquid electrolyte was placed on top of the rinsed separator. Lithium metal foil was placed on top the electrolyte. Stainless steel disc and spring were placed and sealed with the negative top cell case using hydraulic crimper with a pressure of ~ 1000 psi.

In practice, full cells (Figure 3.1b) are used which combines the TiO$_2$ or Li$_4$Ti$_5$O$_{12}$ as anode with a cathode material such as LiCoO$_2$. In full cell, cathode LiCoO$_2$ coated on Al foil was placed on top of positive cell case. Anode (TiO$_2$ and lithium titanate) coated on Cu foil was placed on top of electrolyte/separator.

Electrochemical measurements were carried out using LAND CT2001A battery tester over potential range of 1.0-3.0 V vs Li$^+$/Li using different charge/discharge C-rates.
3.2 Fabrication and characterization of dye sensitized solar cells

The dye sensitized solar cells were fabricated with the structure shown in Figure 3.2. FTO glass substrates were cleaned via ultra-sonication in detergent water, de-ionized water acetone and isopropyl alcohol for 20 mins each. The details are presented in the next section.
Figure 3.2. Cross-sectional structure of dye sensitized solar cell.

3.2.1 Platinum counter electrodes

Platinum coated FTO was used as counter electrode for DSC. A 0.02 M Pt precursor solution was prepared by dissolving $\text{H}_2\text{PtCl}_6\cdot6\text{H}_2\text{O}$ in anhydrous ethanol. Platinized FTO glass as counter electrode was prepared by spin coating Pt precursor solution followed by thermal heat treatment at 400 °C for 15 min in air.

3.2.2 Photoanode

$\text{TiO}_2$ compact layer was prepared by spin coating 0.3 mM titanium isopropoxide precursor solution on cleaned FTO glass substrates at 3000 rpm for 20 secs followed by sintering at 470 °C for 30 min. This was followed by doctor blading a 12 µm thick
nanocrystalline TiO₂ active layer (Solaronix Ti-Nanoxide HT/SP) sintered at 125 °C for 10 min, 250 °C for 10 min and 470°C for 30 min in air. The TiO₂ layer was then immersed in 40 mM TiCl₄ aqueous solution at 70°C for 30 min followed by washing with DI water and ethanol and sintering at 470°C for 30 min in air. Then, the TiO₂ layer was soaked in dye solution containing 0.3 mM Ruthenizer 535-bisTBA dye (N719) in acetonitrile-tert-butanol (1:1 volume ratio) for 24h at room temperature followed by rinsing it in acetonitrile to remove the excess dye.

3.2.3 DSC assembly

The prepared photoanode and the counter electrode were sandwiched using meltonix thermoplastic sealant. A liquid electrolyte consisting of 0.03 M I₂, 0.60 M 1-butyl-3-methylimidaz-olium (BMII), 0.10 M guanidine thiocyanate (GuSCN), and 0.5 M tert-butylpyridine (TBP) in acetonitrile and valeronitrile (85:15 by volume) was injected into the sandwiched structure through precut channels on the sealant. The cell was finally sealed with hot glue. The device cell area was 0.16 cm².

3.2.4 Characterization

An Agilent 8453 UV-Vis spectrophotometer was used to characterize the transmittance of the counter electrodes. The J-V characteristic of the DSCs was investigated under AM 1.5 illumination of 100 mWcm⁻² using a Xenon arc lamp (Newport 67005) with AM 1.5 filter and Agilent 4155C semiconductor parameter analyzer. Cyclic voltammogram (CV) was performed on Ametek VERSASTAT3-200 potentiostat using a Pt wire as counter electrode, an Ag/AgCl as reference electrode and electrode under test as working electrode in an acetonitrile solution containing 10 mM LiI and 0.5 mM I₂ and 0.1
M tetra-\(n\)-butylammonium tetrafluoroborate as supporting electrolyte at a potential scan rate of 0.05 \(V\)s\(^{-1}\). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) characterization was performed using a Hitachi S-4300N SEM. Atomic Force Microscopy (AFM) characterization was carried out using Agilent 5500SPM in tapping mode with Budget Sensors (TAP 300EG) Cr/Pt coated silicon tips with a resonance frequency of \(\sim 300\)kHz and AFM images were analyzed by Gwyddion software.

3.3 Fabrication and characterization of perovskite solar cells

3.3.1. Fabrication of p-i-n perovskite solar cell

The p-i-n perovskite solar cells (PSCs) were fabricated with the structure shown in Figure 3.3. ITO glass substrates were cleaned in detergent water, de-ionized water, acetone and isopropyl alcohol using ultra-sonication for 20 mins each. The cleaned ITO substrate was then plasma treated for 25 mins. Thin layer of PEDOT:PSS was spin coated on top of the ITO at 4500 rpm for 90 sec and sintered at 135 °C for 5 mins. Perovskite solution was prepared by mixing 209 mg of CH\(_3\)NH\(_3\)I and 581 mg of PbI\(_2\) in a binary solvent mixture of 0.7 ml of \(\gamma\)-butyrolactone and 0.3 mL of dimethyl sulfoxide (DMSO) inside the nitrogen glovebox and was kept stirring for 12 h at 70°C on a hot plate. 20 mg of [6,6]–Phenly-C\(_{60}\)-butyric acid methyl ester (PC\(_{60}\)BM) was dissolved in 1 mL of chlorobenzene and kept stirring at 70 °C for 12 h inside a nitrogen filled glovebox.

A perovskite solution was spin coated inside a nitrogen filled glove box on PEDOT:PSS/ITO kept at 70 °C at 750 rpm for 20 s and 4000 rpm for 1 min. After 40 s, during the spin coating, 160 µL of toluene solvent was dropped on to the perovskite film. The film was taken out of the glovebox and kept in air for 5 h to form perovskite crystals. PC\(_{60}\)BM solution was spin coated on top of the perovskite film at 2000 rpm for 40 s and
kept for 15 mins for solvent drying inside the glove box. Precursor solution containing 0.5 mg of rhodamine in 1 mL of isopropanol was then spin coated on top of the PC$_{60}$BM layer at 4000 rpm for 40 s. Finally, silver metal with thickness ~ 100 nm was thermally evaporated on top of the rhodamine. The device cell area was 0.16 cm$^2$.

![Diagram of Perovskite Solar Cell Device Structure](image)

**Figure 3.3.** Perovskite solar cell device structure (p-i-n structure).

3.3.2. Fabrication of n-i-p perovskite solar cell

The n-i-p perovskite solar cells (PSCs) were fabricated with the structure shown in Figure 3.4. Figure 3.4a shows the PSC on a FTO glass substrate. FTO glass substrates were partly etched using diluted HCl solution and zinc powder and were cleaned in detergent water, de-ionized water, acetone and isopropyl alcohol using ultra-sonication for 20 mins each. The cleaned FTO substrate was then UV ozone plasma treated for 25 mins. A thin layer of compact TiO$_2$ layer using a 0.15 M titanium diisopropoxide in anhydrous ethanol was spin coated on top of the cleaned FTO glass at 4500 rpm for 45s and was annealed at 125 °C for 10 min. Mesoporous TiO$_2$ solution was prepared by diluting the Dyesol TiO$_2$ paste in ethanol with 1:6 weight ratio and was ultra sonicated for at least 1 h. A layer of
mesoporous TiO$_2$ was then spin coated at 5000 rpm for 30 s followed by annealing at 100 °C for 10 min and 460 °C for 30 min. Lithium doping of mesoporous TiO$_2$ was done by spin coating a 0.1 M Li-TFSI solution in acetonitrile at 3000 rpm for 30 s followed by annealing at 460 °C for 30 min. After cooling down to 150 °C, the substrates were transferred to the nitrogen glovebox to deposit the perovskite film. The perovskite solution was prepared by dissolving 1M FAI, 1.1 M PbI$_2$, 0.2 M MABr and 0.2 M of PbBr$_2$ in DMF:DMSO (4:1 volume by volume) solvent and addition of 1.5 M CsI dissolved in DMSO in 5:95 volume ratio. The solution was kept at 70°C for 1h and was filtered before use. Perovskite film was spin coated on top of the mesoporous TiO$_2$ in a two-step spin process at 1000 rpm for 10 s and 6000 rpm for 30 s. During the second step, a 100 µL of chlorobenzene was dropped on the spinning substrate 15 s before the end of the second step. The samples were then annealed at 100 °C for 45 min. Spiro-OMeTAD solution was prepared by mixing 70 mM spiro-OMeTAD in chlorobenzene and doped with Li-TFSI acetonitrile solution, TBP and FK209 cobalt salt in acetonitrile in a molar ratio of 0.5, 3.3 and 0.03 respectively. Spiro-OMeTAD layer was spin coated at 4000 rpm for 30s. After that, etching of the sample with Υ-B solution was done for the contacts. This was followed by thermal evaporation of 10 nm of MoO$_3$ layer, DC sputtering of 1 nm Au layer, thermal evaporation of 10 nm of Ag layer and finally 40 nm of MoO$_3$ layer.

Figure 3.4b shows the PSC on a titanium metal substrate. Titanium metal foils were cleaned in detergent water, de-ionized water, acetone and isopropyl alcohol using ultrasonication for 20 mins each. The substrates were then UV ozone plasma treated for 25 mins. The following steps were the same as that of the PSC on FTO glass substrate.

The J-V characteristics of the PSCs were investigated under AM 1.5 illumination of
100 mWcm$^{-2}$ using Xenon arc lamp (Newport 67005) with AM 1.5 filter and Agilent 4155C semiconductor parameter analyzer.

Figure 3.4. Perovskite solar cell device structure (n-i-p structure) with semi-transparent top electrode on (a) FTO glass as bottom electrode (b) Ti metal foil as bottom electrode.
3.4 Photo charging and discharging of discrete Li-ion battery

Figure 3.5 shows the schematic for (a) photo-charging and (b) discharging of discrete Li-ion battery. For photo charging of discrete Li-ion coin cell, the solar cell (PSC and DSC) was illuminated with light intensity of AM 1.5 100 mWcm$^{-2}$ illumination using a Xenon arc lamp. A silicon detector was used to calibrate the light intensity. The bq25504EVM (Texas Instruments) was used as the boost converter. The electrical characteristics of the converter is summarized in Table 3.1. The output of the solar cell was connected to input of the boost converter and the Li-ion cell ($\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiCoO}_2$) was connected to output of the converter for charging. The Li-ion cell was discharged using LAND CT2001A battery analyzer. During charging/discharging, the voltage across the Li-ion cell was measured using the battery analyzer. The Li-ion cell was discharged @ 0.5 C rate between 3.14 -1.0 V.
Figure 3.5. Schematic for (a) photo charging (b) discharging of discrete Li-ion battery.

Table 3.1. Electrical characteristics of the boost converter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Min</th>
<th>Nom</th>
<th>Max</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{IN} (DC)$</td>
<td>0.13</td>
<td>3.0</td>
<td></td>
<td>V</td>
</tr>
<tr>
<td>$V_{IN,Start-up} (DC)$</td>
<td>330</td>
<td></td>
<td></td>
<td>mV</td>
</tr>
<tr>
<td>$V_{ov}$</td>
<td>2.9</td>
<td>3.1</td>
<td>3.3</td>
<td>V</td>
</tr>
</tbody>
</table>
### Maximum power point tracking, Programmed % of open circuit voltage

| MPPT | 78 % |

| Input power range for normal charging | 0.01 mW | 300 mW |

| Minimum cold-start input power to start normal | 10 µW | 50 µW |

3.5 Fabrication and characterization of Li-ion battery on titanium substrate

Li-ion battery on titanium substrate was fabricated with the structure shown in Figure 3.6. Titanium foil substrates were cleaned using ultra-sonication in detergent water, followed by DI water, acetone and isopropyl alcohol each for 20 mins. A slurry containing Li$_4$Ti$_5$O$_{12}$ as active material, super P carbon black as a conductive additive and PVDF as binder (80:10:10 weight ratio) was coated on Ti substrate and vacuum heated at 100 °C for 12 h. A porous polyethylene separator was placed on top of the Li$_4$Ti$_5$O$_{12}$ anode. Cathode LiCoO$_2$/Al was placed on top of the separator. The cell was sealed on three sides with epoxy or scotch tape. The samples were transferred into an argon filled glove box. Suitable amount of electrolyte [1 M LiPF$_6$ dissolved in EC/DMC/DEC (1:1:1 by volume ratio)] was injected from the remaining one side and was sealed using epoxy or scotch tape. Electrochemical characterization was carried out using the LAND CT2001A battery analyzer between potential ranges of 1.0-3.0 V.
Figure 3.6. Li-ion full cell on Ti substrate.

3.6 Fabrication and characterization of integrated PSC/Ti/Li-ion battery

Figure 3.7 shows the structure of integrated PSC/Ti/Li-ion battery. Same procedure was followed to fabricate the n-i-p structured PSC on titanium metal foil as bottom electrode described in section 3.3.2. A thin film battery was fabricated on other side of titanium metal using the procedure described in section 3.5. The only difference was that the slurry of battery anode was heated on a hot plate in air for 30 min to minimize the possible degradation of the perovskite and spiro-OMeTAD layers of the PSC.
Figure 3.7. Cross sectional view of PSC/Li-ion battery integrated device structure.

The integrated device characterization was set up as shown in Figure 3.8. The device was illuminated with AM 1.5 illumination of 100 mWcm\(^{-2}\) using a Xenon arc lamp with AM 1.5 filter from the rear-side of DSC and PSC (Figure 3.8a). A silicon detector was used to calibrate AM1.5 illumination. The voltage across the battery was recorded using a LAND battery tester. The input, output current and input voltage were measured with multimeters.

The input voltage and current were recorded. The integrated device was discharged down to 1V using the LAND CT2001A battery tester once it was fully charged to 3V (Figure 3.8b).
Figure 3.8. Schematic for (a) photo-charging and (b) charging of DSC/Li-ion battery integrated device.
CHAPTER 4: RESULTS AND ANALYSIS

4.1 Electrochemical charge/discharge performance of TiO$_2$ and Li$_x$Ti$_5$O$_{12}$

4.1.1 TiO$_2$

TiO$_2$ with different crystalline phases rutile/anatase P25 TiO$_2$ and anatase TiO$_2$ were tested in half cells to determine the specific capacity of these materials (see Section 3.1). Figure 4.1 shows the specific capacity of cathodes P25-TiO$_2$ and anatase-TiO$_2$ half cells. With half cells, the discharge capacity is observed first since the cell voltage decreases as the cathode under test become lithiated. The anatase-TiO$_2$ had a 1$^{st}$ cycle discharge specific capacity of 250 mAh$_{-1}$ vs 290 mAh$_{-1}$ for the P25 TiO$_2$. The charge specific capacity was 163 mAh$_{-1}$ yielding a coulombic efficiency of 55.4% and 136 mAh$_{-1}$ for the 23$^{rd}$ cycle compared to P25-TiO$_2$ with 130 mAh$_{-1}$ for the 1$^{st}$ cycle (coulombic efficiency of 44.6%) and 64 mAh$_{-1}$ for 23$^{rd}$ cycle. The lower capacity of the P25 TiO$_2$ was attributed to the presence of rutile phase in the P25-TiO$_2$ being less electrochemically active. The practical specific capacity of anatase-TiO$_2$ was only half of the theoretical capacity of 330 mAh$_{-1}$. This was due to the concentration of Li greater than $x = 0.5$ in the Li$_x$TiO$_2$ leading to strong Li-Li interactions [94].
In order to better understand the working of anatase TiO$_2$ as an anode material, a full cell with anatase TiO$_2$ as anode and LiCoO$_2$ as cathode was fabricated. The electrochemical cell charge/discharge reaction is:

$$TiO_2 + LiCoO_2 \leftrightarrow Li_xTiO_2 + Li_{1-x}CoO_2$$

Figure 4.2a shows the cycling performance of anatase TiO$_2$/LiCoO$_2$ based Li-ion coin-type full cell at various C-rates (1 C is equivalent to full charging or discharging in 1 h). A trend of decreasing capacity with increase in charge/discharge rate was observed. A capacity of 152 mAh g$^{-1}$ (1$^{st}$ cycle) to 139 mAh g$^{-1}$ (21$^{st}$ cycle) was obtained for a slow charge/discharge rate of C/10 and 78.6 mAh g$^{-1}$ at a high charge/discharge rate of 2C. The full cell exhibited excellent recovery of 134 mAh g$^{-1}$ equal to 88.4% of the initial capacity at a 0.1 C rate, thus demonstrating good cell stability. Figure 4.2b shows the voltage profiles of the anatase-TiO$_2$/LiCoO$_2$ full cell at various C-rates. For the C-rates the full cell exhibited charge/discharge voltage plateaus at 2.15 V/2.08 V at 0.1 C with the over-
potential increasing with the higher C-rates. For C-rates ≤ 2C, the overpotential was less than 0.35 V. Figures 4.3a and b show energy storage and coulombic efficiencies of the full cell at various C-rates. Energy storage efficiency as high as 87.1% at 0.1 C, 85.2% at 0.2 C, 81.8% at 0.66 C, 77.8% at 2 C and 68.8% at 4 C were observed. Similarly, Coulombic efficiency as high as 97.6% at 0.1 C and 99.8% for 4 C rates were observed.
Figure 4.2. Electrochemical cycling performance of anatase TiO$_2$-LiCoO$_2$ (a) Rate capabilities (b) charge discharge voltage profiles.
Figure 4.3. Efficiencies of anatase TiO$_2$-LiCoO$_2$ full cell (a) energy storage (b) Coulombic.

4.1.2 Li$_4$Ti$_5$O$_{12}$

Figure 4.4a shows the electrochemical cycling performance of Li$_4$Ti$_5$O$_{12}$-Li half cell at various C-rates. The Li$_4$Ti$_5$O$_{12}$-Li cell showed 1$^{st}$ cycle discharge/charge capacities of 160/154 mAhg$^{-1}$ (Coulombic efficiency ~ 96.1%) @ 0.1 C and 149/148 mAhg$^{-1}$ (Coulombic efficiency ~ 99.7%) at the end of 20$^{th}$ cycle @ 0.1 C. This was followed by 5 cycles each of 0.2 C, 0.4 C, 1 C, 2 C and 4 C. The cell exhibited discharge/charge capacities of 147/146
mA\text{h}^{-1} @ 0.2 \text{ C}, 139/139 \text{ mA}\text{h}^{-1} @ 0.4 \text{ C}, 127/126 \text{ mA}\text{h}^{-1} @ 1 \text{ C}, 104/104 \text{ mA}\text{h}^{-1} @ 2 \text{ C}

and @ 74.6/74.6 \text{ mA}\text{h}^{-1} @ 4 \text{ C}. The cell demonstrated good reversibility and stability with retention of 150/150 \text{ mA}\text{h}^{-1} @ 0.1 \text{ C} which accounted for 97\% of the initial capacity.

Figure 4.4b shows half cell discharge/charge voltage plateaus of 1.52/1.56 V at 0.1 \text{ C}. The over-potential increased with increasing C-rates but for C ≤ 2\text{ C}, the over-potential was below 0.15 V. Therefore, \text{Li}_4\text{Ti}_5\text{O}_{12} showed good electrochemical performance and was implemented in a full cell configuration.

Figure 4.5a shows the electrochemical cycling performance of a \text{Li}_4\text{Ti}_5\text{O}_{12}-\text{LiCoO}_2 full cell at various C-rates. Its 1\text{ st} cycle charge/discharge capacities were 167/151 \text{ mA}\text{h}^{-1} (coulombic efficiency ~ 90.6\%) @ 0.1 \text{ C} and 150/149 \text{ mA}\text{h}^{-1} (coulombic efficiency ~ 99.5\%) at the end of 13\text{ th} cycle @ 0.1 \text{ C}. The \text{Li}_4\text{Ti}_5\text{O}_{12}-\text{LiCoO}_2 cell demonstrated capacities of 150/149 \text{ mA}\text{h}^{-1} @ 0.2 \text{ C}, 143/142 \text{ mA}\text{h}^{-1} @ 0.4 \text{ C}, 128/127 \text{ mA}\text{h}^{-1} @ 1 \text{ C}, 105/103 \text{ mA}\text{h}^{-1} @ 2 \text{ C} and 74.4/72.9 \text{ mA}\text{h}^{-1} @ 4 \text{ C}. The cell showed recovery of 148/146 \text{ mA}\text{h}^{-1} which was 96.8\% of the initial capacity. Figure 4.5b shows that the full cell exhibited voltage plateaus of 2.37/2.35 V at 0.1 \text{ C} and for C-rates ≤ 2\text{ C}, the full cell demonstrated a low over-potential of less than 0.1 V. Figures 4.6a and b show energy storage and coulombic efficiencies of the full cell at various C-rates. The energy storage efficiency in \text{Li}_4\text{Ti}_5\text{O}_{12}-\text{LiCoO}_2 cell was as high as 95.7\% for 0.1 \text{ C}, 94.5\% for 0.2 \text{ C}, 93.3\% for 0.4 \text{ C}, 90.5 \% for 1 \text{ C}, 87.2\% for 2 \text{ C} and 82.4\% for 4 \text{ C} rates were observed. Similarly, coulombic efficiencies as high as 99.6\% at 0.1 \text{ C} and 99.4\% at 4 \text{ C} were observed. The higher and stable capacity along with higher storage efficiency makes \text{Li}_4\text{Ti}_5\text{O}_{12}-\text{LiCoO}_2 battery suitable to be used in integrated cell.
Figure 4.4. Electrochemical cycling performance of Li$_4$Ti$_5$O$_{12}$-Li half cell (a) Rate capabilities (b) voltage profiles.
Figure 4.5. Electrochemical cycling performance of Li$_4$Ti$_5$O$_{12}$- LiCoO$_2$ full cell (a) Rate capabilities (b) voltage profiles.
Figure 4.6. Efficiencies of Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ full cell (a) energy storage (b) coulombic.

In summary, Li$_4$Ti$_5$O$_{12}$ had about 10% higher specific capacity and better cycling stability with 10% higher energy storage efficiency in both half and full cells than TiO$_2$ for all C-rates tested. Therefore, Li$_4$Ti$_5$O$_{12}$ was used as the battery electrode material in the integrated cell.
4.2 Photo charging of discrete Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ Li-ion battery

4.2.1 J-V characteristics of DSC and PSC

Figures 4.7a and b show the J-V characteristic curves of a representative PSC (eight studied) and DSC (five studied) respectively. The PSC had a short circuit current density ($J_{sc}$) of 21.99 mA cm$^{-2}$ and open circuit voltage ($V_{oc}$) of 0.96 versus $J_{sc}$ of 19.56 mA cm$^{-2}$ and $V_{oc}$ of 0.68 V for the DSC. Since, the output voltage of these single solar cells was not high enough to charge a 2.4 V Li$_4$Ti$_5$O$_{12}$- LiCoO$_2$ Li-ion cell, DC-DC boost conversion with MPPT was used to increase voltage to the required charging level. The photovoltaic performance parameters are summarized in Table 4.1. The fill factor of the PSC was higher, at 0.68 vs 0.59 for the DSC (see Section 2.3.4). The efficiency of PSC was 14.4% vs 7.8% for the DSC (see Section 2.3.4).

Figure 4.7. J-V characteristics of (a) perovskite solar cell and (b) dye sensitized solar cell.
Table 4.1. Photovoltaic performance parameters of solar cells.

<table>
<thead>
<tr>
<th>Solar cell</th>
<th>Scan</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSC</td>
<td>Forward</td>
<td>21.99&lt;sup&gt;±1.35&lt;/sup&gt;</td>
<td>0.96&lt;sup&gt;±0.00&lt;/sup&gt;</td>
<td>0.67&lt;sup&gt;±0.04&lt;/sup&gt;</td>
<td>14.20&lt;sup&gt;±1.57&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>21.71&lt;sup&gt;±1.28&lt;/sup&gt;</td>
<td>0.96&lt;sup&gt;±0.00&lt;/sup&gt;</td>
<td>0.68&lt;sup&gt;±0.03&lt;/sup&gt;</td>
<td>14.40&lt;sup&gt;±0.96&lt;/sup&gt;</td>
</tr>
<tr>
<td>DSC</td>
<td>Forward</td>
<td>19.56&lt;sup&gt;±1.42&lt;/sup&gt;</td>
<td>0.68&lt;sup&gt;±0.01&lt;/sup&gt;</td>
<td>0.59&lt;sup&gt;±0.02&lt;/sup&gt;</td>
<td>7.89&lt;sup&gt;±0.15&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

4.2.2 Boost converter operation

Table 4.2 summarizes the operating stages of the boost converter during PSC-converter photo-charging of the discrete Li<sub>5</sub>Ti<sub>4</sub>O<sub>12</sub>/LiCoO<sub>2</sub> Li-ion battery for the 1<sup>st</sup> cycle. When the MPPT was inactive, the voltage conversion process had efficiency of 77.0%. When the MPPT was active, the efficiency increased to 88%. The charging stopped at 50 mins at a cut off voltage of 3.14 V.

Table 4.2. Converter operating stages during PSC photo-charging of Li-ion battery.

<table>
<thead>
<tr>
<th>MPPT</th>
<th>Time</th>
<th>Voltage (V)</th>
<th>Converter Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Input to converter</td>
<td>Output of converter</td>
</tr>
<tr>
<td>Inactive</td>
<td>20&lt;sup&gt;th&lt;/sup&gt; sec</td>
<td>0.59</td>
<td>1.80</td>
</tr>
<tr>
<td>Active</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; min</td>
<td>0.73</td>
<td>2.26</td>
</tr>
</tbody>
</table>
4.2.3 Cycling of discrete Li-ion battery using PSC and DSC charging.

Figures 4.8a and b show photo-charge and galvanostatic discharge voltage profiles of a Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ cell charged with a PSC and DSC respectively, for 10 cycles between potential window of 1.0 – 3.0 V followed by 10 charge/discharge cycles using a DC power supply (LAND CT2001A battery analyzer). The PSC-charging and DC supply charging had identical charge/discharge voltage profiles. Also, the DSC-charging had identical charge/discharge voltage profiles as the dc supply charging. This indicated that the photo-charging of the Li-ion battery was as effective as a conventional dc supply charging. It should be noted that the charging voltage had a plateau at ~2.4 V while the discharge plateau was observed at ~2.3 V @ 0.5 C. Therefore the over-potential was very small.

Figures 4.9a and b show the galvanostatic discharge capacities of the Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ cell for PSC and DSC charging respectively. The PSC-charged cell had an initial capacity of 151.3 mAhg$^{-1}$ and 134.6 mAhg$^{-1}$ for 10$^{th}$ cycle. For the dc-supply charging, the cell stored 126.4 mAhg$^{-1}$ (11$^{th}$) and 123.1 mAhg$^{-1}$ (20$^{th}$). This indicated that PSC-charging was as effective as conventional dc charging. The DSC-charged cell had an initial capacity of 166.2 mAhg$^{-1}$ and 160.4 mAhg$^{-1}$ after 10 cycles. This was followed by dc supply charging which had an initial capacity of 160.8 mAhg$^{-1}$ (11$^{th}$ cycle) and 158.2 mAhg$^{-1}$ at the end of the 20$^{th}$ cycle. This indicated that DSC-charging was as effective as conventional dc charging. The lower discharge capacity of the PSC versus the DSC was attributed to the
higher charge current to charge the Li-ion cell. Both solar cell charged cells were able to deliver comparable discharge capacities compared to the dc charging.

**Figure 4.8.** Voltage profiles of Li₄Ti₅O₁₂-LiCoO₂ cell (a) PSC-charging/discharging: red and black lines 1ˢᵗ-10ᵗʰ cycle; dc supply charging/discharging: green and black lines 11ᵗʰ-20ᵗʰ cycles; (b) DSC-charging/discharging: blue and black lines 1ˢᵗ-10ᵗʰ cycle; dc supply charging/discharging: green and black lines 11ᵗʰ-20ᵗʰ cycles.
Figure 4.9. discharge capacity of Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ cell (a) for PSC-charging (10 cycles) followed by dc supply charging for another 10 cycles; (b) DSC-charging (10 cycles) followed by dc supply charging for another 10 cycles.

Figure 4.10a shows the energy storage efficiency ($\eta_{\text{storage}}$) for PSC charging which was as high as 82.1% with an average of 77.2%, while the DC supply charging had $\eta_{\text{storage}}$ as high as 83.3% with average of 82.5%. In comparison, the DSC-charging shown in Figure 4.10b, had $\eta_{\text{storage}}$ as high as 84.9% with an average of 81.1% vs 85.9% for the DC supply charging. The slightly higher energy storage efficiency in DSC-charging was attributed to
lower charge current compared to the PSC-charge current. Figure 4.11a and b show the charging time for PSC and DSC charging respectively compared to DC-supply charging. The DSC charging time was about twice as long as for the PSC. This was due to higher charge current of the PSC owing to its higher power.

Figure 4.10. (a) Energy storage efficiency of PSC-charging; (b) Energy storage efficiency of DSC charging.
Figure 4.11. Photo-charge vs d-supply charge time of the Li-ion cell (a) PSC-charging and (b) DSC-charging.

Figure 4.12 shows the overall efficiency of the PSC and DSC charging for 10 cycles. The PSC-charging demonstrated $\eta_{overall}$ as high as 9.36% and an average of 8.52% while the DSC-charging exhibited as high as 5.62% and an average of 5.27%. The high overall efficiency of PSC charging was attributed to higher perovskite solar cell efficiency leading to higher charging current and lesser charging time. The coulombic efficiency of dc supply
charged Li ion cell was as high as 99.64% after PSC charging and 99.72% after DSC charging as shown in Figure 4.13.

![Graph showing overall efficiency of PSC and DSC charging.](image)

**Figure 4.12.** Overall efficiency of the PSC and DSC charging.

![Graph showing coulombic efficiency of dc supply charging.](image)

**Figure 4.13.** Coulombic efficiency of the dc supply charging.
4.2.4. Maximum power operation of photo charging of Li-ion battery

Figure 4.14a shows the J-V characteristics of a representative PSC for ten cycles. \( V_{\text{max}} \) ranged from 0.737 V to 0.747 V for 1\(^{\text{st}}\) to 10\(^{\text{th}}\) cycles. Figure 4.14b shows the operating voltage during charging when MPPT was active and inactive and was compared to the \( V_{\text{max}} \). During the active MPPT mode, the voltage at which PV operated during battery charging was close to \( V_{\text{max}} \) compared to the inactive MPPT voltage. Figure 4.14c showed that the coupling factor when MPPT was active averaged 0.94 vs 0.83 for inactive MPPT.
Figure 4.14. (a) J-V characteristic curves for different cycles; (b) operating voltage vs cycle number; and (c) PV-battery coupling factor (PV power/P_{max}) during the Li_{4}Ti_{5}O_{12}/LiCoO_{2} cell charging.

4.2.5 Cycling stability of PSC and DSC

Figure 4.15 shows the J-V response of the representative (a) PSC, (b) DSC for 10 charge/discharge cycles. A decrease in J_{sc} was observed for the PSC with increase in number of cycles. This can be attributed to the degradation in perovskite film with exposure to moisture and prolonged illumination. An increase in J_{sc} (V=0) was observed for the initial 6 cycles which was attributed to increased penetration of electrolyte into the TiO_{2} film leading to more TiO_{2}/electrolyte interfaces for dye regeneration. No significant
changes in $V_{oc}$ were observed for both the PSC and DSC. Figure 4.15c shows the efficiency of the PSC and DSC over 10 cycles. The efficiency of the PSC decreased from 14% to 12% while the DSC only decreased from 7.8% to 7.4%. The decrease in the efficiency of PSC was attributed to the degradation in perovskite film with exposure to moisture and prolonged illumination. The photovoltaic performance parameters of the PSC and DSC while photocharging the $\text{Li}_5\text{Ti}_4\text{O}_{12}/\text{LiCoO}_2$ Li-ion coin battery are summarized in Table 4.3 and 4.4 respectively. The fill factor of the PSC decreased from 0.69 to 0.64 for the PSC and from 0.59 to 0.50 for the DSC, indicating that both cells became somewhat more resistive with time.
Figure 4.15. Cycling photovoltaic performance of the solar cells: (a) J-V curve of PSC (b) J-V curve of DSC (c) power conversion efficiency of PSC and DSC over 10 charge/discharge cycles.
Table 4.3. Photovoltaic performance parameters of perovskite solar cell for photocharging Li$_5$Ti$_4$O$_{12}$/LiCoO$_2$ Li-ion battery.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Scan</th>
<th>Jsc $(\text{mAcm}^{-2})$</th>
<th>V$_{oc}$ (V)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>forward</td>
<td>21.99</td>
<td>0.96</td>
<td>0.67</td>
<td>14.23</td>
</tr>
<tr>
<td>0</td>
<td>reverse</td>
<td>21.71</td>
<td>0.96</td>
<td>0.69</td>
<td>14.41</td>
</tr>
<tr>
<td>1</td>
<td>forward</td>
<td>21.38</td>
<td>0.95</td>
<td>0.67</td>
<td>13.68</td>
</tr>
<tr>
<td>1</td>
<td>reverse</td>
<td>21.32</td>
<td>0.95</td>
<td>0.67</td>
<td>13.73</td>
</tr>
<tr>
<td>2</td>
<td>forward</td>
<td>20.73</td>
<td>0.96</td>
<td>0.67</td>
<td>13.48</td>
</tr>
<tr>
<td>2</td>
<td>reverse</td>
<td>20.21</td>
<td>0.96</td>
<td>0.70</td>
<td>13.71</td>
</tr>
<tr>
<td>10</td>
<td>forward</td>
<td>19.84</td>
<td>0.94</td>
<td>0.64</td>
<td>12.03</td>
</tr>
<tr>
<td>10</td>
<td>reverse</td>
<td>19.44</td>
<td>0.94</td>
<td>0.66</td>
<td>12.13</td>
</tr>
</tbody>
</table>

Table 4.4. Photovoltaic performance parameters of DSC for photo-charging Li$_5$Ti$_4$O$_{12}$/LiCoO$_2$ Li-ion battery.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Jsc $(\text{mAcm}^{-2})$</th>
<th>V$_{oc}$ (V)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19.56</td>
<td>0.68</td>
<td>0.59</td>
<td>7.89</td>
</tr>
<tr>
<td>1</td>
<td>21.06</td>
<td>0.69</td>
<td>0.53</td>
<td>7.77</td>
</tr>
</tbody>
</table>
In summary, the use of a single solar cell, which simplifies manufacturing, in combination with a MPPT boost converter can be employed to charge a Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ Li-ion battery. The efficiency of PSC was 14.2% vs 7.8% for the DSC. The boost converter had average efficiency of 88% with MPPT active. It was estimated that with inactive MPPT, the charging efficiency would be about 77%. PSC-charging led to 19% lower discharge capacity and 5% lower storage efficiency than DSC-charging which was attributed to higher PSC charging current. With MPPT led PSC-charging had 9% overall efficiency for PSC-charging vs 5% for the DSC. This was attributed to the higher efficiency of the PSC. The PSC efficiency decreased by 2.2% while DSC was more stable with only a decrease of 0.4% for 10 charge/discharge cycles.

4.3 Photovoltaic performance of PSC with transparent top electrode

4.3.1 Optical and electrical characteristics of the transparent top electrode

The opaque metal top electrode used in conventional PSC was replaced with a dielectric-metal-dielectric (DMD) structure. DMD structures have the capability to increase the transmission through a metal film due to interference effects provided by the two dielectric layers. Such DMD structures have been employed as transparent conductors for various applications such as optoelectronic devices and semi-transparent windows. The DMD structure employed in this work consists of a MoO$_3$/Au/Ag/MoO$_3$ as shown in Figure 16a. MoO$_3$ was used due to its hole transport properties. It also provides a good nucleation surface for metal film deposition. Figure 16b shows the transmittance spectra of the semi-
transparent top electrode with different layers. The thin silver (Ag) electrode with only 10 nm thickness is only 30% transparent at 550 nm wavelength. The use of Au seed layer increased the transmittance at 550 nm to 55%. The DMD structure showed a transmittance of 80% at 550 nm wavelength with decreasing transparency towards the infra-red region. The increase in transparency in visible region can be attributed to the optical interference created by the use of MoO$_3$ on bottom and Au/Ag layer on top. The top MoO$_3$ served as an anti-reflection coating.

A trade-off exists between the transparency and the conductivity of a metal top electrode. The use of thinner metal electrode is suitable to achieve higher transmittance, however thinner metal electrode has higher resistance. The thin 10 nm Ag electrode is highly resistive with kΩ range resistance. This can be attributed to the tendency of the atoms to bound to each other rather than to the substrate which leads to the Volmer-Weber (island) growth mode which leads to a non-continuous Ag film as can be seen in Figure 16c. Ag film is very rough with RMS value of 11.2 nm (Figure 16d). The use of 1 nm gold (Au) film as seed layer underneath the Ag leads to a very compact Ag film as seen in Figure 16e. Roughness decreased to 1.55 nm (Figure 16f). This can be attributed to the Frank-van der Merwe (layer-by-layer) growth mode of Ag instead of island mode during evaporation enabled by the use of Au seed layer which resulted in a continuous film. This is due to the energetically more favorable interaction between Ag and substrate than Ag-Au since Au has higher surface area. This leads to a conductive Ag film as shown by the CS-AFM image in Figure 16g, where the film exhibits high surface current all over the film.
Figure 4.16. DMD transparent top electrode. A) thickness of the different layers used; B) Optical transmittance of the top electrode with different layers; AFM topography images and 3D-views of (C, D) Ag and (E,F) Au/Ag; G) CS-AFM images of Au/Ag film.
4.3.2. I-V performance of PSCs with the semi-transparent top electrode

Figure 4.17 shows the J-V characteristic curve of PSCs with the semi-transparent DMD as top electrode and FTO and Ti as bottom electrodes. The PSCs were evaluated with front (FTO side) and rear illuminations (DMD side). Conventional PSCs with FTO as bottom and Ag as top electrodes was also fabricated for comparison. The photovoltaic performance parameters are summarized in Table 4.5.

The rear illuminated PSC on FTO with DMD as top electrode had average efficiency of 8.12% compared to its front illumination which had 13.83%. The lower efficiency can be attributed to the lower transmittance of the DMD top electrode compared to the FTO bottom electrode as supported by the Jsc values. The PSC with titanium as bottom substrate had average efficiency of 8.10% which is comparable to that of the rear illuminated PSC with FTO substrate.
**Figure 4.17.** J-V characteristics of PSCs with Ti (as bottom) and DMD (as top) electrodes versus PSCs with FTO (as bottom) and DMD and Ag (as top) electrodes.

**Table 4.5.** Photovoltaic performance parameters of PSCs with Ti (as bottom) and DMD (as top) electrodes versus PSCs with FTO (as bottom) and DMD (as top) electrodes.

<table>
<thead>
<tr>
<th>Bottom/Top electrodes</th>
<th>Illumination side</th>
<th>Voc (V)</th>
<th>Jsc (mA cm⁻²)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO/Ag</td>
<td>Front - FTO</td>
<td>0.947 ± 0.026</td>
<td>23.51 ± 0.68</td>
<td>0.622 ± 0.030</td>
<td>13.83 ± 0.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.97)</td>
<td>(23.62)</td>
<td>(0.658)</td>
<td>(15.08)</td>
</tr>
<tr>
<td>FTO/DMD</td>
<td>Front - FTO</td>
<td>1.02 ± 0.014</td>
<td>21.41 ± 0.96</td>
<td>0.507 ± 0.045</td>
<td>11.13 ± 1.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.03)</td>
<td>(23.45)</td>
<td>(0.559)</td>
<td>(13.42)</td>
</tr>
<tr>
<td>FTO/DMD</td>
<td>Rear - DMD</td>
<td>0.99 ± 0.029</td>
<td>15.01 ± 0.48</td>
<td>0.544 ± 0.048</td>
<td>8.12 ± 0.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.00)</td>
<td>(16.01)</td>
<td>(0.590)</td>
<td>(9.44)</td>
</tr>
<tr>
<td>Ti/DMD</td>
<td>Rear - DMD</td>
<td>0.916 ± 0.027</td>
<td>15.4 ± 0.67</td>
<td>0.57 ± 0.04</td>
<td>8.10 ± 0.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.94)</td>
<td>(15.37)</td>
<td>(0.634)</td>
<td>(9.16)</td>
</tr>
</tbody>
</table>
4.3.3. Cycling performance of Li$_4$Ti$_5$O$_{12}$/LiCoO$_2$ Li-ion battery on titanium

Figures 4.18a shows specific capacity vs cycle number for a Li$_4$Ti$_5$O$_{12}$/LiCoO$_2$ Li-ion thin film cell compared to a coin cell. The thin film cell had a discharge capacity of 102.3 mAh$^{-1}$ for the 1$^{st}$ cycle which was comparable to 103.5 mAh$^{-1}$. For the 24$^{th}$ cycle, the thin film cell had 76 mAh$^{-1}$ discharge capacity compared to 95.6 mAh$^{-1}$ for the coin cell. The lower capacity was attributed to the inadequate sealing of the thin film cell leading to exposure of the electrolyte.

Figure 4.18b shows the coulombic efficiency vs cycle number for the Li$_4$Ti$_5$O$_{12}$/LiCoO$_2$ Li-ion thin film cell compared to a coin cell. The thin film cell had coulombic efficiency of 77.8% for the 1$^{st}$ cycle comparable to 81.3% for coin cell. For the following cycles, the coulombic efficiency of thin film cell was comparable to that of the coin cell. Figure 4.18c shows the energy storage efficiency vs cycle number for the Li$_4$Ti$_5$O$_{12}$/LiCoO$_2$ Li-ion thin film cell compared to a coin cell. The thin film cell had energy storage efficiency of 68.6% for the 1$^{st}$ cycle compared to 72.5% for coin cell. For the following cycles, the energy storage efficiency for the thin film cell was around 85% which was 1% lower than that of the coin cell.
Figure 4.18. (a) specific capacity (b) coulombic efficiency (output charge/input charge) (c) energy storage efficiency (output energy/input energy) of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiCoO}_2$ Li-ion thin film cell versus coin cell.
In summary, thin film Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ Li-ion batteries on titanium substrates had comparable specific capacity and efficiency in the 1$^{st}$ 10 cycles to a coin cell. The subsequent 1% decrease in capacity per cycle was attributed to electrolyte leakage.

4.5. Photo-charging/discharging of integrated PSC/ Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ Li-ion battery

4.5.1. Charge/discharge performance of integrated cell

Figure 4.19a shows photo-charge and galvanostatic discharge voltage profiles of a PSC/Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ integrated cell for five cycles between potential window of 1.0 – 3.0 V followed by five charge/discharge cycles using a DC power supply (LAND CT2001A battery analyzer). The integrated PSC-charging and DC supply charging had identical charge/discharge voltage profiles. This indicated that the photo-charging of the integrated cell was as effective as a conventional dc supply charging. It should be noted that the charging voltage had a plateau at ~ 2.4 V while the discharge plateau was observed at ~2.3 V @ 0.5 C. Therefore the over-potential was very small. Figure 4.19b shows the galvanostatic discharge capacities of the integrated cell with PSC charging and DC charging. The integrated cell had capacities of 154.4 mAh/g (1$^{st}$ cycle) to 154.4 mAh/g (5$^{th}$ cycle) for PSC charging followed by 134.8 mAh/g (6$^{th}$ cycle) to 134.0 mAh/g (10$^{th}$ cycle). Therefore, the PSC charging showed similar capacities as the DC charging. The slight difference might be due to the slight difference between the charging currents.
Figure 4.19. (a) Voltage profiles of Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ cell: PSC-charging/discharging: red and black lines 1$^{\text{st}}$-5$^{\text{th}}$ cycle; DC supply charging/discharging: blue and green lines 6$^{\text{th}}$-10$^{\text{th}}$ cycles; (b) discharge capacity over number of charge/discharge cycles.

Figure 4.20a shows the overall efficiency of the PSC/Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ integrated cell. The integrated cell had $\eta_{\text{overall}}$ as high as 4.21 % with an average of 4.15%. However, the efficiency was lower than that of the PSC and Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ discrete charging system with 8.5% average efficiency. One of the reasons to attribute is the different device
structure used in integrated cell. The discrete system used standard FTO substrate as the bottom electrode and used front illumination (FTO side) with more light reaching the perovskite absorber layer while, the integrated system used metal Ti substrate which required rear illumination (from top electrode side). However, the top electrode developed is not as transparent as FTO and in addition, the hole transport layer (Spiro-OMeTAD) absorbs a significant amount of ultraviolet light. Figure 4.20b shows the storage efficiency of the PSC/Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ integrated cell. The average storage efficiency was 81.3% which is very close to that of the DC charging of the integrated cell with 83.0% and higher than that of the discrete PSC charging with 77.2%. Figure 4.20c shows the coulombic efficiency of the integrated cell under DC charging. The average value was 99.1% which is comparable to that of the coin cell.
Figure 4.20. Efficiency of PSC/Li₄Ti₅O₁₂-LiCoO₂ integrated cell (a) Overall efficiency; (b) Storage efficiency and (c) Coulombic efficiency.
Figure 4.21 shows the rate capability of the PSC/LIB integrated cell. The integrated cell demonstrated discharge capacity of 147.7 mAhg\(^{-1}\) at 0.66 C and 55.5 mAhg\(^{-1}\) even at high 5.32 C rate. After the cycling at high 5.32 C rate, the integrated cell demonstrated excellent recovery of 148.8 mAhg\(^{-1}\) accounting to retention of ~100 % of the initial capacity at 0.66 C rate.

![Graph showing rate capability](image)

**Figure 4.21.** Rate capability of the PSC/LIB integrated cell.

Figure 4.22a shows the J-V response of the integrated cell. Not much difference in \(V_{oc}\) and \(J_{sc}\) was observed. Figure 4.22b shows the solar cell efficiency over five charge/discharge cycles and Table 4.6 summarizes photovoltaic performance parameters of PSC/Li-ion battery integrated cell. The FF decreased from 0.59 before cycling to 0.56 after 5\(^{th}\) cycle. The average efficiency decreased from 6.64 % before cycling to 5.84 % after 5\(^{th}\) cycle. This can be attributed to the degradation of the perovskite film over cycles due to continuous exposure to light.
Figure 4.22. Cycling photovoltaic performance of the PSC/Li-ion battery integrated cell: (a) J-V curve (b) average power conversion efficiency over number of charge/discharge cycles.
Table 4.6. Photovoltaic performance parameters of PSC/Li-ion battery integrated cell.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Scan</th>
<th>Jsc (mAcm⁻²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>Efficiency (%)</th>
<th>Average efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Forward</td>
<td>12.69</td>
<td>0.922</td>
<td>0.532</td>
<td>6.24</td>
<td>6.64</td>
</tr>
<tr>
<td>0</td>
<td>Reverse</td>
<td>12.63</td>
<td>0.944</td>
<td>0.590</td>
<td>7.04</td>
<td>6.32</td>
</tr>
<tr>
<td>1</td>
<td>Forward</td>
<td>13.15</td>
<td>0.842</td>
<td>0.484</td>
<td>5.36</td>
<td>6.00</td>
</tr>
<tr>
<td>1</td>
<td>Reverse</td>
<td>13.02</td>
<td>0.933</td>
<td>0.546</td>
<td>6.63</td>
<td>6.23</td>
</tr>
<tr>
<td>2</td>
<td>Forward</td>
<td>12.97</td>
<td>0.866</td>
<td>0.486</td>
<td>5.47</td>
<td>6.47</td>
</tr>
<tr>
<td>2</td>
<td>Reverse</td>
<td>12.92</td>
<td>0.966</td>
<td>0.599</td>
<td>7.47</td>
<td>6.03</td>
</tr>
<tr>
<td>3</td>
<td>Forward</td>
<td>13.15</td>
<td>0.855</td>
<td>0.451</td>
<td>5.07</td>
<td>5.59</td>
</tr>
<tr>
<td>3</td>
<td>Reverse</td>
<td>12.81</td>
<td>0.9</td>
<td>0.529</td>
<td>6.10</td>
<td>5.83</td>
</tr>
<tr>
<td>4</td>
<td>Forward</td>
<td>13.29</td>
<td>0.877</td>
<td>0.486</td>
<td>5.67</td>
<td>6.07</td>
</tr>
<tr>
<td>4</td>
<td>Reverse</td>
<td>12.96</td>
<td>0.922</td>
<td>0.541</td>
<td>6.46</td>
<td>5.95</td>
</tr>
<tr>
<td>5</td>
<td>Forward</td>
<td>12.64</td>
<td>0.855</td>
<td>0.463</td>
<td>5.01</td>
<td>5.84</td>
</tr>
<tr>
<td>5</td>
<td>Reverse</td>
<td>12.54</td>
<td>0.944</td>
<td>0.563</td>
<td>6.67</td>
<td></td>
</tr>
</tbody>
</table>

4.5.2. Maximum power point operation of the integrated cell

Figure 4.23a shows the J-V characteristics of the PSC/Li₄Ti₅O₁₂-LiCoO₂ integrated cell for five charge/discharge cycles. V_{MPP} ranged from 0.688 V to 0.689 V for 1ˢᵗ to 5ᵗʰ cycles. Figure 4.23b shows the operating voltage during charging when MPPT was active and inactive and was compared to the V_{MPP}. During the active MPPT mode, the voltage at
which PV operated during battery charging was close to $V_{MPP}$ compared to the inactive MPPT voltage. Figure 4.23c showed that the coupling factor when MPPT was active averaged 0.935 vs 0.716 for inactive MPPT.
Figure 4.23. (a) J-V characteristic curves for different cycles; (b) operating voltage vs cycle number; and (c) PV-battery coupling factor (PV power/P_{max}) during the Li_4Ti_5O_{12}/LiCoO_2 cell charging.

4.5.3. Statistics of the photo-charge/discharge performance of the integrated cell

Figure 4.24 shows the statistics of (a) overall and (b) energy storage efficiencies of PSC/Li_4Ti_5O_{12}-LiCoO_2 integrated cell over three different batches. The average overall efficiency was 3.3% with a standard deviation of 0.63. The average overall efficiency for each of the batches were 2.66% (batch 1), 3.06% (batch 2) and 4.15% (batch 3). As can be seen in Figure 4.24b, the energy storage efficiency for photocharging was comparable to that of the dc charging. The average storage efficiency over the three batches was 79.92% with a standard deviation of 2.336 for photocharging and 81.94% with a standard deviation of 3.854 for dc charging. For photocharging, the average storage efficiency for each of the batches were 81.63% (batch 1), 76.61% (batch 2) and 81.50% (batch 3) while, dc charging exhibited 86.04% (batch 1), 76.78% (batch 2) and 83.01 (batch 3).
Figure 4.24. Statistics of (a) overall efficiency and (b) energy storage efficiency of PSC/Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ integrated cell over three different batches.
4.5.4 Storage time equivalent of the photo-rechargeable systems

For additional analysis of the storage requirements of the photo-rechargeable system, requirement based on actual fluctuating irradiance data was assessed. For this analysis, irradiance data of a fluctuating day (June 19, 2013) was selected as shown in Figure 4.24a. The irradiance was averaged over 1 min interval. 10%/min ramp rate was used as the limit. Figure 4.24b shows the actual ramp rates observed. A positive ramp rate as high as 46.5 and a negative ramp rate as high as 55.6 were observed with a total number of violations of 115.

![Irradiance profile](image1)
![Ramp rate](image2)

**Figure 4.25.** (a) Irradiance profile of June 19, 2013; (b) Ramp rate (%/min) indicating number of violations.

Figure 4.25a shows the generated PV power and PV power meeting the 10%/min ramp rate. When the positive rate of change of the generated PV power per minute was higher than the 10%, the battery would be charged with the excess power to satisfy the limit. Meanwhile, when the negative rate of change was higher than the 10%, the battery would be discharged to supply the shortage power to satisfy the limit. Figure 4.25b shows the battery power and battery energy required to satisfy the limit. The positive battery power indicates battery charging and negative battery power indicates battery discharging.
The battery energy was calculated by integrating the battery power with time. The battery power required for this day was 0.365 mW and battery energy was 0.0502 mWh. This battery energy is equivalent to 181 secs of capacity.

Similarly, storage time equivalent of other ramp rates was calculated and is shown in Figure 4.26. Imposing lower ramp rate limits led to requirement of longer storage time or higher battery energy. The storage time equivalent for the different ramp rates is tabulated in Table 4.7.

Figure 4.26. (a) Actual PV power profile and PV power profile satisfying the 10%/min ramp limit; (b) Required battery power and energy to meet the limit.
Figure 4.27. Storage time equivalent to meet the different ramp rates.

Table 4.7. Storage time equivalent for different ramp rate limits.

<table>
<thead>
<tr>
<th>Ramp rate limits (%/min)</th>
<th>Storage time equivalent (secs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1273</td>
</tr>
<tr>
<td>2</td>
<td>927</td>
</tr>
<tr>
<td>5</td>
<td>376</td>
</tr>
<tr>
<td>10</td>
<td>150</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>40</td>
<td>8</td>
</tr>
<tr>
<td>50</td>
<td>3.3</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 4.8 shows the storage time equivalent for different photo-rechargeable systems. The time equivalent of the reserve energy capacity provided by the PSC/Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ integrated cell was calculated to be 524 s. The average energy stored was 0.883 mWh, the area of the battery was 1.21 cm$^2$, energy storage density $E_{storage}$ was 0.73 mWh/cm$^2$ and the PV cell active area was 0.18 cm$^2$ with an average efficiency of 6.07%. Power density, $P$ of the PV cell was 6.07 mW/cm$^2$. The time equivalent was therefore 433 s which was higher than the required 243 s as calculated in section 2.4 to meet the 10%/min ramp rate limitation.

**Table 4.8. Summary of the storage time equivalent of the photo rechargeable systems.**

<table>
<thead>
<tr>
<th>Design</th>
<th>Solar cell</th>
<th>Energy storage density (mWh/cm$^2$)</th>
<th>PV Power density (mW/cm$^2$)</th>
<th>Time equivalent (secs)</th>
<th>Time equivalent (secs) for 10%/min (practical scenario)</th>
<th>Time equivalent (secs) for 10%/min (worst case scenario)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolated charging</td>
<td>PSC</td>
<td>1.10</td>
<td>13.34</td>
<td>297</td>
<td>150</td>
<td>243</td>
</tr>
<tr>
<td></td>
<td>DSC</td>
<td>1.32</td>
<td>7.76</td>
<td>612</td>
<td>150</td>
<td>243</td>
</tr>
<tr>
<td>Integrated charging</td>
<td>PSC</td>
<td>0.73</td>
<td>6.07</td>
<td>433</td>
<td>150</td>
<td>243</td>
</tr>
</tbody>
</table>

The PSC/Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ integrated cell had storage time $>$ 181 secs to satisfy the desired 10%/min ramp rate and also could satisfy even lower ramp rate of 5%/min which required 424 secs.
CHAPTER 5: CONCLUSIONS

5.1 Summary

A significant share of energy still comes from traditional fossil fuels which generate pollution and are non-renewable. Solar photovoltaics (PV) is a very promising renewable energy technologies as it is abundant and pollution-free. However, the major drawback of PV power is its intermittency, as PV power output depends on solar irradiance which is not constant due to clouds and random sun periods. This suggests the use of energy storage to smooth out this intermittency. Traditionally, PV energy generation and storage is based on PV panels and batteries or other storage technologies such as pumped hydro, working as independent units electrically connected via long distance electric wires. However, such systems are bulky, inflexible, require significant space, and undergo energy loss through external wires and expensive. Integration of batteries with solar modules by combining the two functions of solar PV energy generation and energy storage can reduce overall PV system costs and increase the practicality of PV power.

Integration of photovoltaic cells with supercapacitors demonstrated the feasibility of combined photovoltaic energy generation and storage, but the supercapacitors had low energy storage capacity and the cost of supercapacitor ($/kWh) was high. The use of a single junction silicon solar cell integrated with silicon nanowire/ lithium ion battery on a common Si substrate was also investigated, however, solar cell charging of the battery was not studied. An integrated rechargeable thin film battery combined with five commercial amorphous silicon thin film solar cell in series was also examined but energy storage capacity was low. A dye sensitized solar cell was integrated with a lithium-air battery but the integrated device required an external charging source to fully charge the battery.
Recently, a dye sensitized electrode integrated into a redox battery was reported but with low solar cell efficiency. A tandem dye sensitized PV cell with integrated Li-ion battery as energy storage was also demonstrated but had a complex structure due to multiple PV cells; low efficiency due to a mismatch between the PV cell and battery; and low storage capacity due to the use of a TiO$_2$ nanostructure as a battery electrode material which had high power density but low energy density.

There is a need for an efficient integrated photovoltaic rechargeable energy storage system that is cost effective. The goal of this research was to develop an integrated photovoltaic/energy storage device that: is simple to manufacture (roll to roll) by using a single solar cell; is more efficient by using MPPT with boost converter; and has higher energy storage using suitable and compatible battery electrode materials.

An integrated dye sensitized solar cell/Lithium ion battery could consist of a solar cell on top of a Li-ion battery with a shared titanium substrate/common electrode and a boost converter to match the PV voltage to the battery voltage. For this structure, the DSC would require rear-illumination so light would be incident from the counter electrode side. The requirements for the integrated cell also include suitable boost converter, transparent counter electrode for the PV cell, a battery anode compatible with common substrate and thin film Li-ion battery. An integrated PSC/Li-ion battery would have the same operation and requirements as the integrated DSC/Li-ion battery device. PSCs have higher efficiency and voltage than DSCs but are less stable. Islanded grids with a high penetration of renewables desire a 10% per minute maximum ramp rate on PV plants connected to the grid. The required reserved energy capacity to meet this ramp rate would be 67.5 mWh/W, which is equivalent to 0.0675 h or 243 s. The typical Li-ion coin cell battery can provide
951 s and has a thickness, excluding battery cases of 0.2 mm. In thin film form, thickness would be about the same and similar to the thickness of a DSC cell.

Battery anode materials compatible with common electrode substrate (titanium) such as titanium dioxide (TiO$_2$), lithium titanate (Li$_4$Ti$_5$O$_{12}$) were investigated for high energy specific capacity, low over-potential and stable cycling performance. The performance of DSCs, PSCs with a MPPT boost converter using discrete single solar cells to charge batteries were investigated to determine if the MPPT boost converter can provide the boost function with maximum PV power. A transparent Pt/AZO counter electrode was investigated for efficient back illumination of the DSC integrated cell. Similarly, semi-transparent DMD structure top electrode was investigated for efficient back illumination of the PSC integrated cell. PSCs and DSCs on titanium substrate were fabricated and characterized for optimization of the solar cell efficiency. Likewise, thin film flexible lithium ion batteries on titanium substrate were fabricated and characterized for optimization of the cycling performance. Integrated PV/energy storage devices using DSCs, PSCs and Li-ion battery were fabricated and characterized using MPPT boost converter.

Li$_4$Ti$_5$O$_{12}$ had about 10% higher specific capacity and better cycling stability with 10% higher energy storage efficiency in both half and full cells than TiO$_2$ for all C-rates tested. Therefore, Li$_4$Ti$_5$O$_{12}$ was used as the battery electrode material in the integrated cell. The efficiency of PSC was 14.2% vs 7.8% for DSC. The MPPT led to over 9% overall efficiency for PSC-battery charging vs 5% for the DSC. This was attributed to the higher efficiency of PSCs. PSC efficiency decreased by 2.2% while DSC was more stable with a decrease of 0.4% for 10 cycles studied. DMD structure as top electrode for transparent
PSCs demonstrated transmittance of 80% in visible regime and rear efficiency of 8.1% for Ti-PSC versus 8.12% for FTO-PSC. The integrated PSC-battery had $\eta_{\text{overall}}$ as high as 4.2% with an average of 3.46%. This overall efficiency of the integrated cell was lower than the discrete PSC charging of the Li-ion coin battery. This was attributed to the lower efficiency of the rear illuminated PSC in the integrated cell. The storage efficiency of the integrated cells was comparable to that for discrete charging of Li-ion coin battery. MPPT converter efficiency of the integrated cells was similar to that of the discrete DSC charging of the Li-ion coin battery. A decrease in the discharge capacity of the integrated cells was observed similar to that of the thin film battery studied separately. A simple analysis demonstrating the use of the integrated cell for PV ramp rate application showed that the PSC/Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ integrated cell had storage time > 181 secs to satisfy the desired 10%/min ramp rate and also could satisfy even lower ramp rate of 5%/min which required 424 secs.

5.2 Conclusions

This was the 1$^{st}$ report of an integrated thin film single solar cell with a thin film Li-ion battery charged using a boost converter with MPPT. The highest efficiency of 4.2% and 1.55% was obtained for an integrated PSC/Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ cell. This integrated device had less complex fabrication, higher storage capacity and was more efficient in comparison to previous reports on integration with a dye sensitized solar cells. The Li-ion battery used in this work had some electrolyte leakage, therefore the technology need further work on stability. A high overall efficiency of 9.36% was obtained for a perovskite solar cell charging a Li$_4$Ti$_5$O$_{12}$-LiCoO$_2$ Li-ion battery as separate units. However, an economic analysis of the use of single solar cell with converter to charge battery was not
done. This was also the 1st report of use of DMD structures as a transparent top electrode for perovskite solar cells employing a metal substrate.

Despite the intensive research on low cost alternative PV to silicon, it is still the dominant technology since the cost of the silicon cells has dropped significantly. Therefore, the use of silicon solar cells (a-Si for roll to roll processing) and use of thin film technology such as CIGS for PV-battery integration may be more practical. PSC are at an early development stage and have achieved high efficiency, but stability is a major concern. If this problem is solved then, use of PSC for PV-battery integration would be the choice of priority. Flexible integrated design is possible with the use of PSC with a solid state battery design.

5.3 Future Work

Future work should include optimization of the integrated cell to prevent battery electrolyte leakage by use of solid state Li-ion batteries. Thin film CIGS/Li-ion battery integrated cell can also be studied. Another task will be to study the response of the integrated cell during light intermittency.
References


[77] A. Paolella *et al.*, "Light-assisted delithiation of lithium iron phosphate nanocrystals towards photo-rechargeable lithium ion batteries," *Nature Communications*, vol. 8, p. 14643, 2017.


