Chapter

Physicochemical Approaches for Thin Film Energy Storage Devices through PVD Techniques

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Abstract

For the fabrication of thin films, Physical Vapor Deposition (PVD) techniques specified greater contribution than all other deposition techniques. Laser Ablation or Pulsed Laser deposition (PLD) technique is the one of most promising techniques for the fabrication of thin films among all other physical vapor deposition. In particular, flexible thin-film energy storage fabrication PLD plays an important role due to its special parameters such as fine thickness control, partial pressure atmospheric condition, pulsed repetition rate, in-situ annealing and microstructure optimization. Very recently, thin film supercapbatteries have been broadly studied, in which the battery and supercapacitor based electrodes are combined to obtain a high specific power and specific energy density and extended cycle stability. In order to fabricate thin film supercapbatteries, electrodes that have a large potential window, high capacitance, and capacity performance are vastly desired. Thus, the presented chapter represents an important enhancement in the growth of economical and eco-friendly thin flexible supercapbatteries and confirms their potential in sensible applications such as transport electronics devices and other gadgets.

Keywords: pulsed laser deposition, thin film supercapbatteries, micro electronics devices, semi solid state electrolytes, volumetric specific capacities

1. Introduction

Increasing energy consumption, rising human population and global warming has raised the necessity to progress alternative energy sources and Electrochemical Energy Storage (EES) devices for futuristic necessities. Further, intensifying demand on high-performance EES for portable microelectronic devices and hybrid electric vehicles has designed giant research thrust in the search for a novel diversity of energy storage devices [1–3]. Most of the modern microelectronic are intended to work on EES such as batteries, Supercapacitors and Hybrid Supercapacitors or Supercapbatteries. In particular, small-scale hybrid devices possessions have become vital requirements for diverse insistent purposes such as biomedical devices and portable electronics. With the intent, EES systems have been well-thought-out as an appropriate power sources for innumerable hands-on potential applications owing to the fast charging/discharging rate capability and exceptional stability. Instantaneously, extensive development in EES technology proposes to interest on the electrochemical performance of electrode materials,

electrolytes, and strategy of the devices [4–6]. To make specially, the active material should be sort out in a cost-effective manner for receiving high specific energy and specific power at low cost. However, to meet the greater necessities of upcoming systems, Researchers need to expand their performance by designing novel materials with high energy and power density concurrently. In the past few years, widespread activities have been defined to emphasize for the capable and simplistic progressions to fabricate thin, stretchable, and signifigant solid-state flexible batteries and supercapacitors, which are well thought-out as one of the opted candidates for most promising power sources in many of the portable and microelectronic applications [7–9].

The thin film energy storage devices like batteries and supercapacitors for satisfying the energy inevitabilities to balance both power and energy densities. In typical supercapbatteries contain two types of energy storage mechanism in a single device that which explicit pseudo capacitive (Faradaic) nature and other one is battery behavior [10, 11]. For emerging flexible thin film energy storage devices fabrication to form thin film electrodes there are variety of coating methods such as Electrochemical deposition (ED) [12], Physical Vapor Deposition (PVD) [13], Chemical Vapor Deposition (CVD) [14], sol–gel coating method, spray coatings, dip coating and innovative thin film coating systems such as Atomic Layer Deposition (ALD) [15] and Pulsed Laser Deposition (PLD) [16] have been employed in the noticeable arrival of thin flexible electrode assemblies. Frequently, the growth of micro and nanostructure coatings in thin film form are more suitable for flexible energy device applications and the most important benefits as the electrode is binder and conductive free in its structural design. This chapter deals with the electrochemical behavior of vanadium pentoxide (V_2O_5) and tungsten trioxide (WO_3) thin films using PLD as well as thermal Evaporation technique used as different kind of Flexible thin film energy storage devices such as symmetric Supercapacitor and Supercapbatteries. Author demonstrated Transition metal oxides (TMOs) based thin film electrodes for flexible energy storage system rather than bulk electrodes. This chapter shows the recent influence of the TMO based thin films fabricated through PVD techniques for thin film Supercapacitors / Supercapbatteries. Also an example for anode (WO_3) and cathode (V_2O_5) which based on the use of massive scale to micro / Nano scale structures to enhance the electrochemical properties of new energy systems with appropriate cost. This approach will be defined and delivered for enlightening device performances with extended cycle life of thin film Supercapacitors / Supercapbatteries based on the principal of electrochemical solid state redox reactions.

1.1 Thin film energy storage

The expansion of flexible and portable electronics harmfully demands thin flexible and wearable energy storage devices (ESDs) that preserve both high energy and power density with their greater durability and flexibility to influence a vast wearable energy storage systems. Thus, extensive work have been devoted to emerging various types of flexible, stretchable and portable rechargeable supercapacitors (SCs) and batteries [17, 18]. Plentiful development has been accomplished in terms of thin film electrode material design and flexible device structure along with their electrochemical performance. With new type of ESDs, excluding outdated tests applied on supercapacitors, batteries and now supercapbatteries how to evaluate their "viability" and "portability" growths as a concern. Twisting and extending tests are the most used approaches to validate to the stability of flexible thin and stretchable energy storage devices, respectively [19, 20].

1.2 Why thin film energy storage

Since the scalability, a growth of micro electrochemical power sources with thin film structural design opens the approach for powering moderated devices such as electronic chip units, Biomedical implantable devices and credit card/ debit cards, and individual sensors systems. The technology of the thin film is useful for understanding the essential properties of the electrode active materials of energy storage system such as Supercapacitors along with lithium ion batteries (cathodes, anodes and solid state electrolytes) free of polymeric binder and carbonaceous preservative [21, 22]. More importantly in the form of thin film energy storage depends up on some specific features like morphology, size, thickness, pore volume etc., here author report why thin film energy storage device important requirement of society.

i. For making of compact sized devices, synthesis of active electrode materials at a bulk scale may not be appropriate reason of the giving out issues. These demands for the requirement for thin film fabrications, which can simplify the expansion of compact devices and significantly binder less for electrode fabrications.

ii. The Bulk SCs have two main drawbacks that boundary their application for transportable electrical and electronic devices. To begin with, the device manufacture consists of high-cost packing materials and device fabrication techniques to avoid the possible leakage of electrolytes, as most of the organic electrolytes are highly toxic and corrosive nature. Furthermore, it is challenging to construct small and flexible thin SC devices using liquid electrolytes attributable to the packaging problem.

iii. Smooth thin films are highly adhesive, can also be used as a reference material for exploration of the morphology's effect on the performance of electrode active materials, as the dimensions, pore volume, surface area and shape of particles influence the physicochemical properties expressively.

Additional imperative factor for the improved attention on thin-film battery resources is their applicability in micro-Lithium Ion Batteries (LIBs). The micro-scaling of devices is ongoing to compact the sizes of devices in addition to their energy demand, which makes many separate applications practicable, if micro-LIBs can be used for the power supply. These energy storage systems can be useful in different fields, such as biomedical implantable devices, laptops-on-chip, or micrometer-sized sensor systems.

1.2.1 Supercapacitors

Supercapacitors (SCs) have significant attention in past years owing to their high power density, long stability of cycle life and ability to bridge gap of the power and energy density between conventional capacitors, fuel cells and Lithium ion batteries (LIBs) Ragone plot of all kinds of energy storage is displayed in **Figure 1**. SCs retain extremely reversible ion adsorption /desorption on the surface of the electrode, nevertheless suffer with low energy density. An evolution of SC with its advantages of greater power density more than batteries, larger energy density delivers than the conventional capacitors, and exceptional durability, is playing an extraordinary role as a favorable candidate to come across this ongoing demand for high efficient EES and to throw out extended necessity on unsustainable fossil fuels [10, 23, 24].

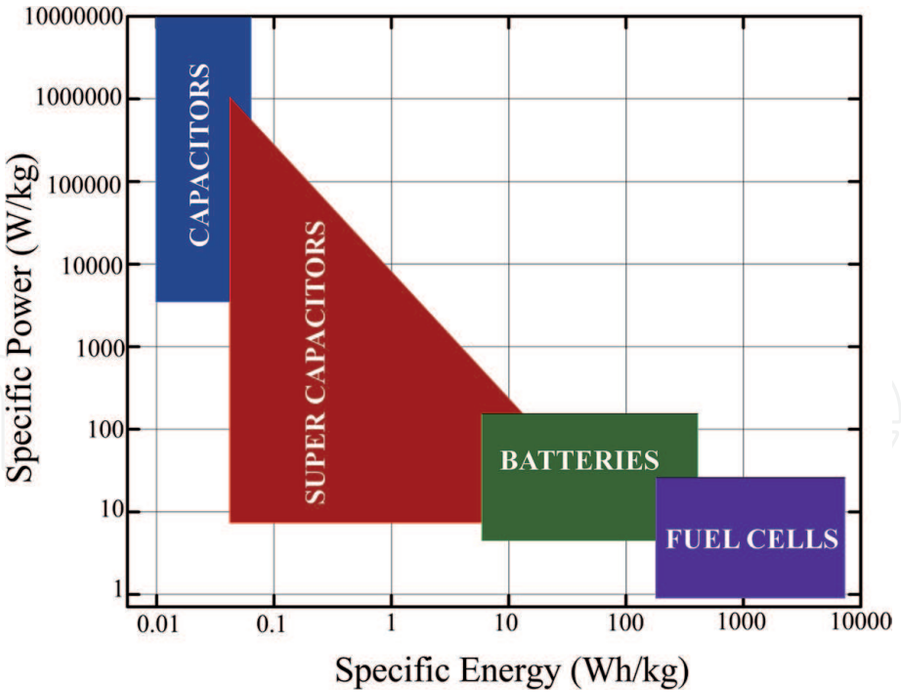

Figure 1.
Ragone plot comparison with all kinds of energy storage system.

Therefore, a single EES device, which can instantly provide high energy density and high power outputs with long lost, is an extremely desirable.

1.2.1.1 Symmetric Supercapacitor

Symmetric supercapacitor is typically assembled by two identical electrodes such as anode and cathode electrodes. The symmetric supercapacitors having limited operating voltage of an aqueous electrolyte up to 1.23 V being restricted by water decomposition, while using organic electrolyte whose voltage window can extend up to 2.7 V. Thin film supercapacitors (TFSCs) have materialized as a new class of electrochemical energy storage device and have considerable attention in recent years. TFSCs make their presence as one of the greatest hopeful energy storage devices attributable to their high power density, outstanding stability, light weight and are easy to handle. Nevertheless, the performance of predictable designs deteriorates extensively as a consequence of electrode and electrolyte exposure to atmosphere along with mechanical distortions for the case of flexible systems [25]. TFSCs are flexible and easily reconfigurable supercapacitors display great potential for application in portable electronics. Moreover, Flexible all-solid state supercapacitors are well-thought-out as a state-of-the art power supply for diminished electrical and electronic devices because they proficiently avoid the leakage of harmful electrolytes, which frequently happens in traditional aqueous electrolyte-based supercapacitors [26, 27]. Numerous challenges limit their applications, such as the thin film composite fabrication process and the underprivileged interfacial compatibility among the electrode and the solid state electrolyte. In contrast to conventional SCs, flexible solid-state SCs have more than a few important benefits containing small size, low weight, exceptional reliability, and an extensive range of practical temperatures. TFSCs hold abundant promise for use as energy storage devices for flexible, stretchable and wearable electronics [7].

Recently the author group reported V_2O_5 thin film symmetric SC was fabricated using thermal evaporation technique shown in **Figure 2a**.In this work Ni foam substrate was used as a flexible current collector electrode, Flexible V_2O_5 thin film

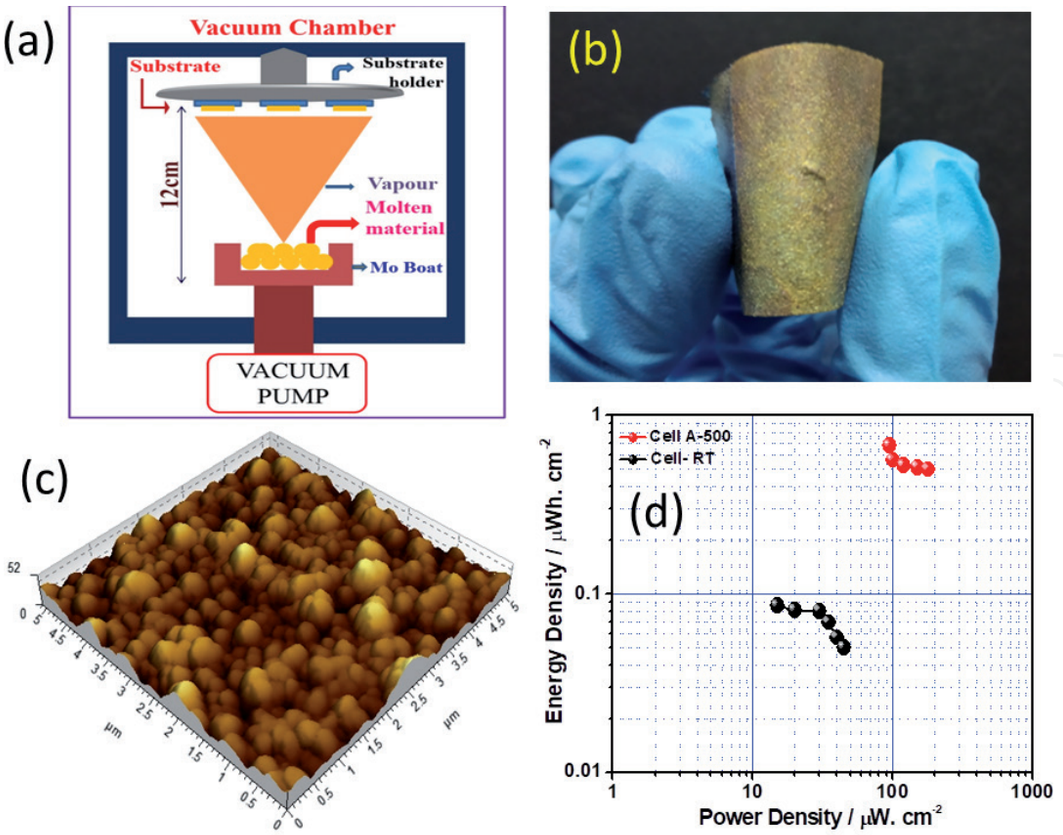

Figure 2.
(a) Schematic diagram of thermal evaporation technique; (b) photographic image V_2O_5 thin film annealed at 500°C at CSIR-CECRI, India; (c) AFM 3D topographical morphology of V_2O_5 thin film; (d) Ragone plot of V_2O_5 symmetric capacitors (Reprinted with permission from Ref. [46]. Copyright 2019 American Chemical Society) .

electrodes were subjected to observed in a post annealing temperature at 500°C is shown in a **Figure 2b** (photographic image of Ni foam at CECRI, India). The V_2O_5 annealed at 500°C thin film was highly conducting nature owing to larger grain size, it is clearly indicated from the Atomic Force Microscopic 3D topographic image as shown in **Figure 2c**. Further author's group compared energy and power density of two symmetric V_2O_5 thin film devices such that As-prepared thin film electrode device (Cell-RT) and Annealed at 500°C thin film electrodes device (Cell A-500) is presented in **Figure 2d**. The cell A-500 delivered the maximum areal energy density around 0.7 μWhcm^{-2} which is fourteen times greater than as prepared cell-RT (0.05 μWh cm^{-2}) [28]. Later author's group reported two symmetric thin film SCs using PLD, here this work V_2O_5 and WO_3 thin film symmetric SCs was fabricated and successfully demonstrated various electrochemical investigation such as Cyclic Voltammogram (CV) and Galvanostatic Charge and Discharge (GCD). The CV curves of both V_2O_5 and WO_3 symmetric SC devices is exposed **Figure 3** a & c reached the maximum voltage up to 1.2 V in a solid state PVA-KOH electrolyte, it is clearly indicated the decomposition appeared each devices above 1.0 V. To avoid this issue, author fixed the voltage window in GCD curve at different current densities of V_2O_5 and WO_3 thin film symmetric SCs such as 1.0 V and 0.8 V as revealed in **Figure 3c** and **d** [28].

1.2.1.2 Asymmetric Supercapacitor

Potential window of the symmetric SCs be necessary more or less limitation due to similar materials (same potential widow) used for fabrication, this is one of important difficulty of symmetric SCs. On the way to overwhelm these

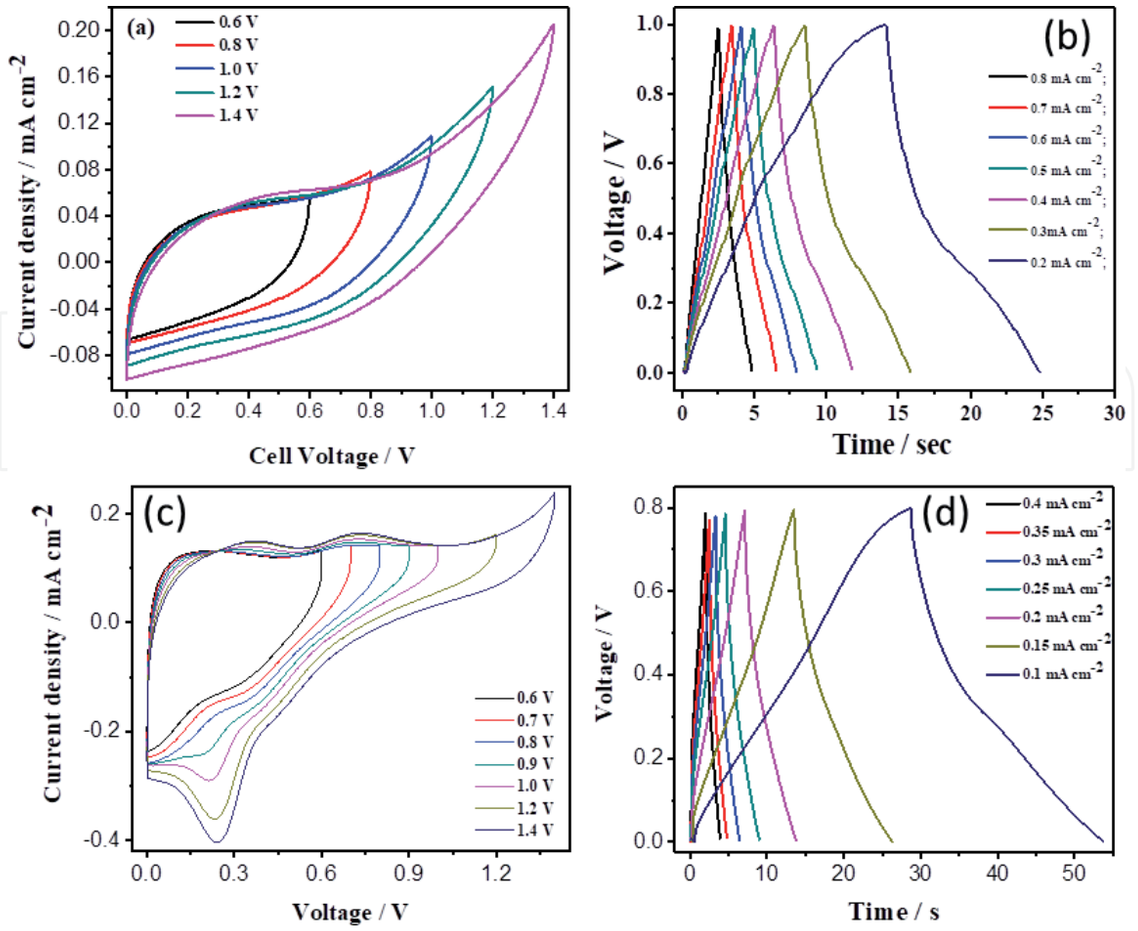

Figure 3.
(a) CV curves V_2O_5 symmetric capacitor in different voltage window; (Reprinted with permission from Ref. [46]. Copyright 2019 American Chemical society) (b) GCD curves V_2O_5 symmetric capacitor in different current densities; (c) CV curves WO_3 symmetric capacitor in different voltage window; (d) GCD curves V_2O_5 symmetric capacitor in different current densities (Reprinted with permission from Ref. [28]. Copyright 2020 Royal Society Chemistry).

issues two dissimilar materials along with different potential widow based active materials are used in device fabrication for extending the voltage window. Asymmetric supercapacitors (ASCs) retain higher theoretical energy density than conventional symmetric SCs have complicated widespread consideration throughout the recent years. Still, there is a huge capacity gap between the two electrodes obviously restrict higher specific energy [29]. Flexible thin film electrodes capacity depends on mass, surface area and thickness of the films, can make the capacity balanced even though optimizing parameters such as weight, volume and thickness of the electrodes. One of the important footnote for several applications, in specific for portable micro electronic devices and hybrid vehicles, the volumetric specific energy is more important than gravimetric specific energy [30, 31].

1.2.2 Batteries

Conventional Li-ion batteries ensuring abound with limitations such that LIB constructed organic electrolytes are highly toxic, corrosive nature and only be handled with glow box atmospheric condition. To avoid this difficulties, solid state batteries (SSB) will be necessary the potential to progress the next generation of energy storage devices over the promises of greater energy density and healthier protection. The main perseverance of solid state electrolyte empowers

the predictable of flimsy lithium metal as the anode despite the fact replacing the frequently used inflammable organic electrolyte [32]. Even though the ionic conductivity of definite solid state electrolytes must come together taking place and in some incidents exceeded organic liquid electrolytes, their extensive application has remained inadequate by the excessive interfacial resistance sandwiched between the solid electrolyte and electrode [33, 34].

1.2.2.1 Thin film batteries

Thin film based LIBs ought to be established loads of wellbeing in consequence of their potential applications as overbearing power sources for micro-electronic devices such as smart cards, sensors and implantable medical devices since many thin film micro-batteries adopt flimsy metal lithium as an anode, development of the cathodes with high energy density becomes significant [35]. All Lithium ion batteries have certain limitations such as spreading out fire, explosive nature of hazards chemicals and overheating at the positive as well as negative electrodes take place while the charge–discharge process in a liquid electrolyte sealed in a metal container [36]. Consequently, all-solid state battery with a solid electrolyte should be very safe and reliable. The schematic stack diagram of solid state thin film battery is shown in **Figure 4** [17]. The thin film SSB consisting anode, cathode and solid state electrolyte in the form of thin film to avoids explosive hazards chemicals, leakage free devices and flexible nature. The electrodes used in thin-film batteries are limited to those that exhibit little volume change during Li ion insertion /deinsertion, since expansion-contraction is restricted in solid-state films [37]. For thin film SSB device fabrication PVD techniques play vital role especially PLD is unique tool for solid state electrolyte deposition in thin film SSB device production. Accordingly, Gil Yoon et al. stated $LiCoO_2$ thin film cathodes fabricated by PLD and the thin film cathode delivered maximum areal capacity 25 μAh cm^{-2} [38]. Kuwata et al. demonstrated solid state electrolyte based $LiCoO_2$ thin film cathodes by PLD and the solid state battery delivered maximum capacity 9.5 μAh cm^{-2} [39]. Park et al. reported Si thin film prepared by PLD for micro battery application, Si thin film electrode delivered maximum areal capacity about 96.7 μAh cm^{-2} [40]. Previously reported literatures reveals that the thin film electrodes used as a coin cell type battery devices. Thus, Author reveals that the thin film based coin cell fabrication by using schematic diagram of thin film battery as displayed in **Figure 5**.

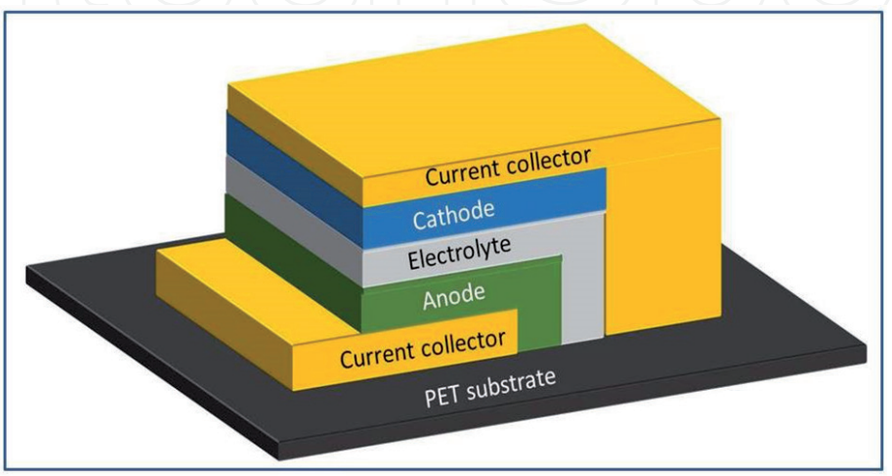

Figure 4.
Schematic stack diagram of solid state thin film battery.

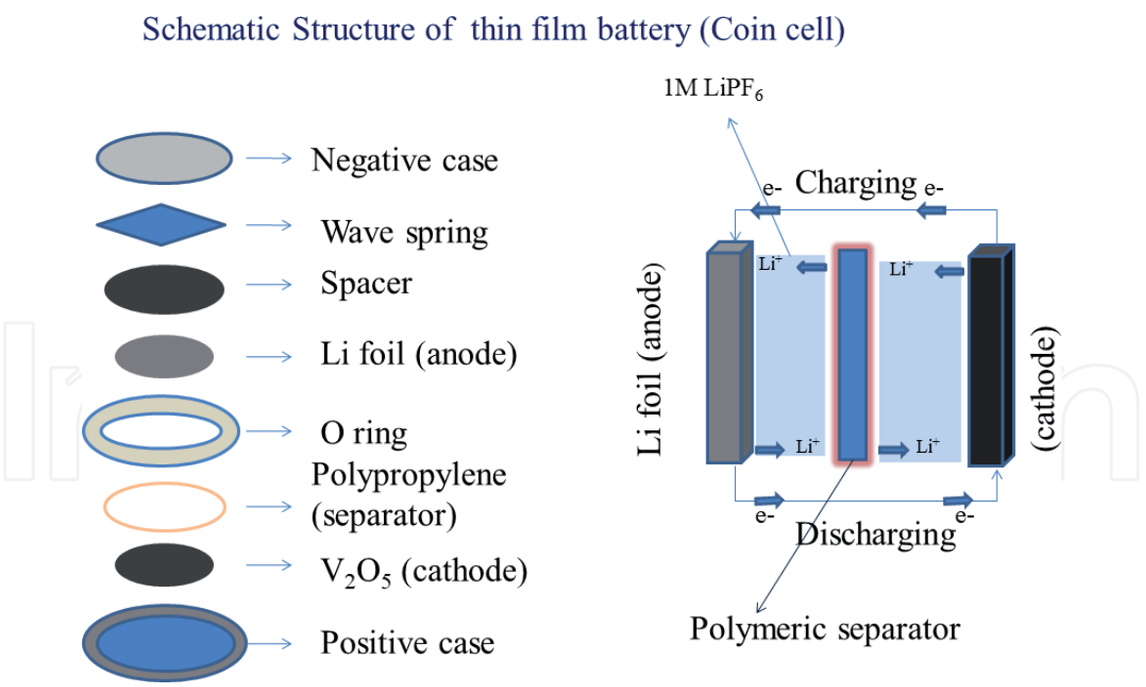

Figure 5.
Schematic representation of structure of thin film battery.

1.2.2.2 From supercapacitor to supercapbatteries

SCs still have restricted ordinary -life practical application for that their energy density is not comparable to with that of other EESs such as batteries, which the criteria of upcoming energy necessity is far away from adequate to extent. This status spurs ground breaking consequence in the design and preparation of novel hybrid EES that could combining two mechanism is the more advantages than batteries and SCs, which is denoted as supercapbatteries (=supercapacitor + battery) [41]. Therefore, hybrid energy storage devices known as supercapbatteries are rising as a replacement to overwhelm the disadvantage of conventional supercapacitors and batteries, by combining the benefits of each of them, which are superior power and energy density, respectively. A hybrid device is combined by two electrodes with different energy storage mechanism, such as Electric Double Layer Capacitor (EDLC) and faradaic processes; this hybridization of two electrodes could form use of their compatible potential window to increase the voltage window of the device, hence attempt has been made to attain high energy density without yielding constitutional power delivery and very long cycle life of SCs. It deserves that the electrochemical performance of Supercapbattery is nearly attendant to the reasonable design of electrode materials, particularly battery-type materials which deliver large capacity developed from dynamical Faradaic redox reactions. Consequently, the consideration of novel battery-type materials based on various Nanostructures has become a research focal point to encourage the electrochemical performance of Supercapbatteries [42, 43]. Recently Author group designed thin film based supercapbatteries by using PLD. In this work, the fabricated supercapbattery device [28] made by two Transition Metal Oxides (TMOs) such as WO_3 and V_2O_5, here WO_3 exhibited pseudo-capacitive behavior and V_2O_5 revealed the battery type behavior. Further, cyclic voltammograms of thin film supercapbattery consisting of WO_3 as negative electrode and V_2O_5 as positive electrode and their three electrode configuration is presented in **Figure 6a**. The thin film supercapbattery device can reached voltage window 1.8 V (**Figure 6b**) in an aqueous 2 M KOH electrolyte and the thin film device reached 1.6 V in a solid state PVA-KOH gel electrolyte.

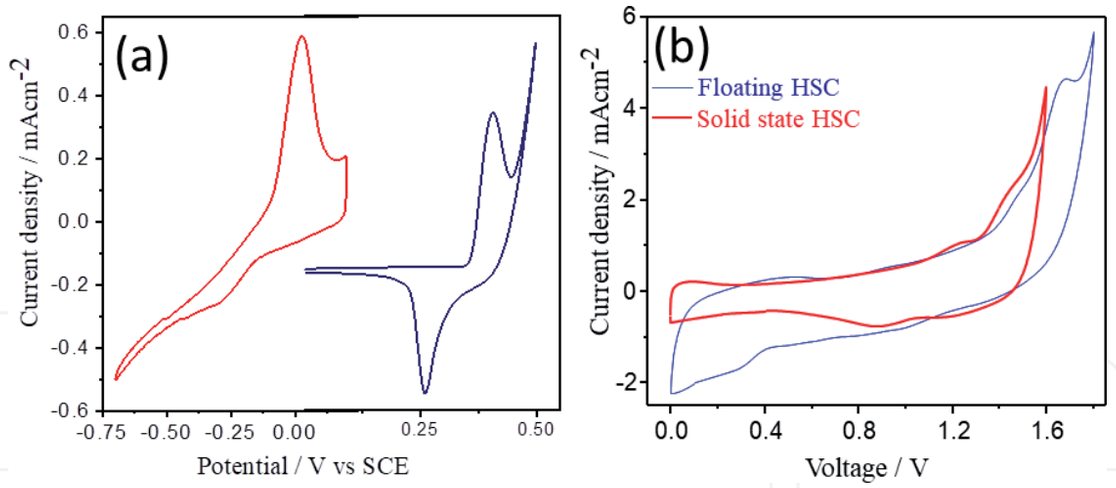

Figure 6.
(a) CV curve combination V_2O_5 and WO_3 thin films in a three electrode configuration; (b) CV curve comparison of Supercapbattery both aqueous and solid state electrolytes.

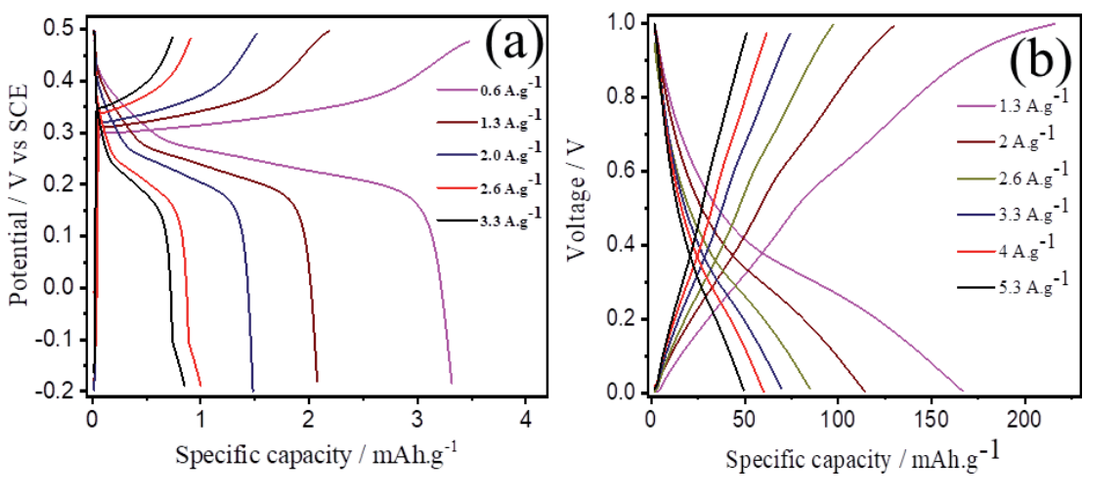

Figure 7.
(a) Charge discharge profile of V_2O_5 thin film in a three electrode configuration; (b) charge discharge profile of V_2O_5 symmetric supercapacitor.

1.2.2.3 Supercapbatteries in an electrochemical approach

Supercapbattery devices having high effective battery type electrode materials, which is determined slow kinetics, rate performances quit low and less number of cycling stability. Supercapbattery devices construct the larger potential of battery materials such they are fashionable redox active nature permitting faradaic reaction processes with high energy density materials are appropriate for positive electrodes and pseudo-behavior materials are highly suitable for negative electrodes [41, 43]. In this similarity, author reported the electrochemical investigation of V_2O_5 thin film electrode in a three electrode configuration delivered maximum capacity of 3.25 mAh g^{-1} at a current density of 0.6 A g^{-1} as displayed in **Figure 7a**. Even though V_2O_5 thin film symmetric device exhibited maximum capacity 160 mAh g^{-1} at a current density of 1.3 Ag^{-1} as shown in **Figure 7b**.

Furthermore, a thin film supercapbattery device was assembled by using PLD process, in this work V_2O_5 as a cathode because of it is perform battery nature and WO_3 as an anode as it deliver pseudo capacitive behavior. The supercapbattery device shows the better redox behavior in a semi solid state electrolyte was used for fabrication, the thin film device exhibit the maximum voltage of 1.6 V clearly which

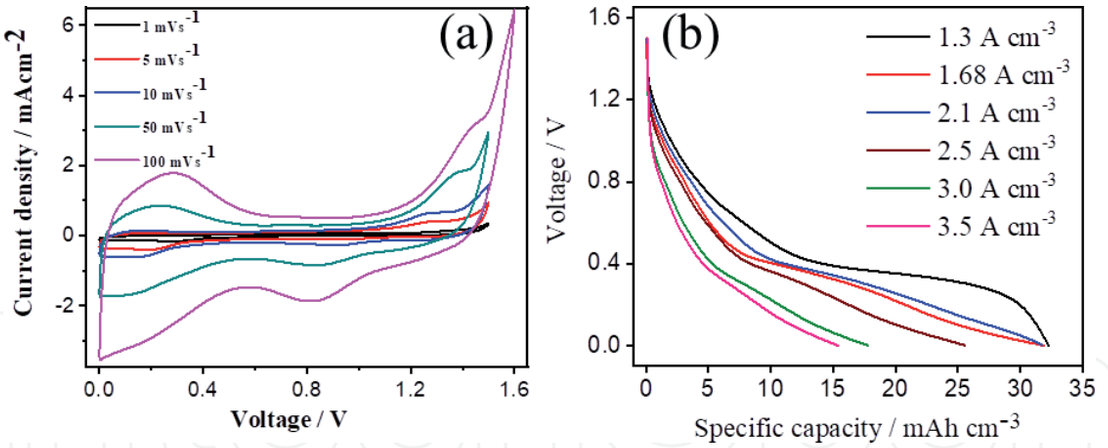

Figure 8.
(a) CV curve of thin film supercapbattery device in different sweep rates; (b) discharge profile for the thin film supercapbattery device.

indicates CV and discharge profile curves shown in **Figure 8a** and **b**. The supercapbattery device showed excellent rate performance as displayed in **Figure 8b**; the device delivered maximum volumetric discharge capacity of 32 mAh cm^{-3} at a current density of 1.3 A cm^{-3}. This is the first thin film supercapbattery energy storage was reported by using PLD system [28]. The agreeing thin film supercapbattery device fabrication cost is very low due to author used alkaline based PVA-KOH electrolyte and the total mass of 0.2 to 0.5 mg of active materials used for thin film supercapbattery fabrication. Therefore, thin film supercapbattery device is economical and eco friendly in nature.

1.3 Why PVD techniques for flexible energy storage fabrication

In the past few years ago EES device assembling electrodes such as anodes and cathodes fabrication frequently used approaches like Slurry, Hydrothermal and other synthesis methods ensuring sufficient draw backs for instance the active materials should be very high, low stability owing to require for proper binder, bulky electrodes may not appropriate for micro electronic device fabrication, larger size EES devices, essential proper complex mixture of active materials. To overwhelmed these scenario flexible thin film electrodes fulfill due to less active materials necessary for fabrication for instance compared bulky electrodes 2 to 10 μm thickness thin film electrodes fabrication required active mass of 0.2 to 1 mg, in attendance no necessity of binder required flexible thin film electrode fabrication because thin film electrodes are highly adhesive in nature. Thin film electrodes capable of assembling any miniaturized energy storage devices such as planar Micro- Nano supercapacitors and fiber based energy storages. Intended for emerging flexible thin film energy storage devices, there are numerous thin films coating methods for the occasion of Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), spray coatings, Electrochemical Deposition (ED) and liberal coating methods such as Atomic Layer Deposition (ALD) and Pulsed Laser Deposition (PLD) have been employed in the noticeable appearance of thin flexible electrode fabrications. Frequently, the expansion of micro and nanostructure coatings in thin film form are more suitable for flexible device applications and the major improvement for the thin film electrode is binder and conductive free in its architecture. As we identify that together with the different physical vapor deposition (PVD) techniques such as Thermal evaporation, e-beam evaporation, Magnetron sputtering and PLD, in predominantly PLD is matchless for the intention that its competency to functioning in very high pressure of background reactive gases. The recompenses of the PLD process are flexibility, fine

thickness control, high growth rate, quick evaporation and compatible vaporization. PLD also plays an enthusiastic role in influencing the microstructure and phases of the numerous active TMOs and metal sulfides based electrode materials used in the electrode assemblies. In summary, thin film electrode fabrication by PVD techniques are most promising tool to enhance the materials crystalline nature, providing better nano structure with good adhesive properties than films prepared by other techniques.

1.3.1 Thermal Evaporation

Thermal evaporation coating system is a modest technique among all PVD system for thin film fabrication. The schematic diagram of thermal evaporation technique is displayed in **Figure 2a**. In this technique molten material in the form of powder, foils, pellets and salts for thin film fabrication with the help of boats, crucibles and buckets. Usually boats and crucibles made up of molybdenum and tungsten metals owing to they have high meting points. Thermal evaporation technique functioning under the principle of law of conservation such that electrical energy converted to the thermal energy, meanwhile molten materials transferred to one state to another state. Intended for deposition process occurs while applying the current through the boats or crucibles molten material at a particular temperature it goes condensation state to deposit in the form of solid state film on the substrate. In this thermal evaporation technique for a thin film deposition normally used molten material such as some metals foils Al, Cu, Ni, etc. and some metal oxides those materials having low melting points. Recently yen lei et.al approached thermal evaporation technique to form SnS_2 thin film for flexible photodetector applications. Ziran Ye et al. reported Ag film on the liquid surface by using thermal evaporation technique for Surface Enhanced Raman scattering (SERS) application [44]. Hailin Hu et al. fabricated Zinc oxide thin film by using this method for Planar Perovskite Solar Cell application [45]. Author group reported V_2O_5 thin film supercapacitor prepared by thermal evaporation technique [46]. In conclusion, from the literature thermal evaporation technique is one of the simplest techniques for thin film fabrication for multiple applications also the suitable candidate for thin film energy storage fabrication.

1.3.2 Magnetron sputtering

Thermal evaporation technique has temperature limitation with deposition occurs only for materials having melting point below 1200°C. To overcome this issue Magnetron Sputtering (Schematic diagram is shown in **Figure 9**) coating unit as suitable PVD technique for thin film fabrication attributable to its ensuring more or less special features such as temperature limitations depending on the melting point, thickness control coating unit, easy way to deposit metals, semiconducting materials, ceramic materials and some polymers. In thermal evaporation technique composite thin films cannot be deposition at instant time as it depends on melting point deposition occurs sequentially, In contrast Magnetron sputtering Composite materials deposition happens for instantaneous due to its having multiple target (cathodes) holders. The deposition due to influence of ion bombardment of growing films intensely inspirations their microstructure, and for that reason their physical properties of the film should be changed. Ion bombardment may perhaps intensification to the movement of atoms on the surface of growing film, which effects in increasing the reordering probability of atoms. The thin film process parameters of the magnetron sputtering while deposition is displayed the **Table 1**. All metal oxides, metal sulfides, metal nitrides and metal alloy

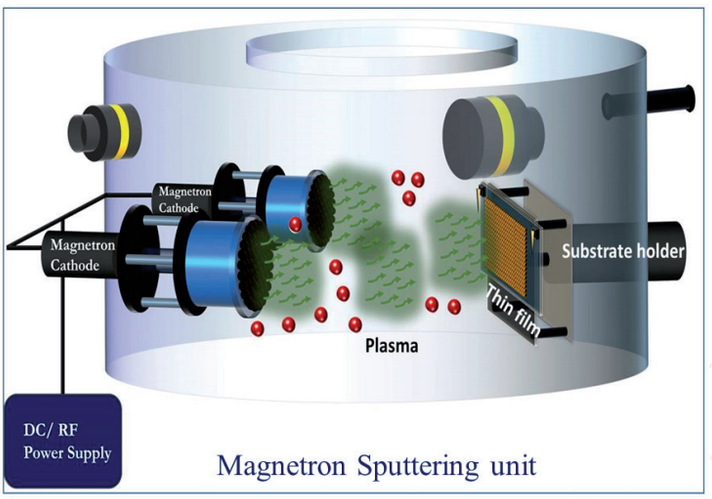

Figure 9.
Schematic diagram of magnetron sputtering unit.

Process parameters	Range
Temperature	RT – 500 °C
Partial pressure	(mbar) 10^{-6}, 10^{-4}, 10^{-2}
Inlet gases	Ar, N_2, O_2, Acetylene (C_2H_2), Methane (CH_4)
Distance between cathodes and substrate holder	5 cm
Power supply	DC power supply Typically 2000 W RF Power supply Radio frequency: 13.56 MHz Forward power: 0 – 1200 W Reflected power: 0 – 1200 W Biasing -50 V to -1000 V
Vacuum pressure	1×10^{-6} (mbar)
Substrate rotation Speed	1 to 10 rpm
Target size	2″ inch & 3″ inch (depending upon cathode)

Table 1.
Thin film preparation parameters of magnetron sputtering coating unit.

composites materials based thin films by the promising method to deposit magnetron sputtering for innumerable applications, in particularly more than a few reports available based on energy storage applications. Hyunsik Im et al. reported CuO_2 thin film fabricated by using magnetron sputtering for supercapacitor and electro catalyst [47]. Z. Zhang et al. stated molybdenum oxide thin film fabricated via magnetron sputtering for micro supercapacitor application [48]. Zhoucheng Wang et al. demonstrated CrN symmetric thin film supercapacitor with the help of magnetron sputtering unit, and the symmetric device exhibited excellent cycling stability [49]. Zhoucheng Wang et al. studied binder-free titanium nitride thin film electrodes prepared by magnetron sputtering unit for supercapacitors [20]. From the literature magnetron sputtering technology is one of advanced coating system even if comparable lot advantages than thermal evaporation technique, and magnetron sputtering is situated promising tool for flexible thin film electrode fabrications.

1.3.3 Pulsed Laser Deposition

Thermal evaporation and Magnetron sputtering units having few limitations merely two to three composite materials deposited at prompt time. To overwhelmed constraint Laser ablation or PLD (schematic of PLD is shown in **Figure 10a**) had better established to be an unique furthermost suitable techniques for the deposition of thin films comprising an unpredictable through composite stoichiometry. Also PLD has some inimitable advantages such that in-situ temperature controller, partial pressure atmospheric condition, layer by layer coatings, varying the ablation rate exclusively to develop micro/ Nano structured thin film, even this system delivers sufficient microstructure variation and morphologies necessitate for superior electrochemical performance as the most important benefits in PLD are larger deposition rate, precise thickness control unit, capability to functioning in high reactive background gases pressures, and fewer nonconformity from the target composites [50]. The thin film fabrication process parameters of the PLD is exposed in **Table 2**. In this technique Krypton Fluorine (KrF) premixed laser source was used to ablate

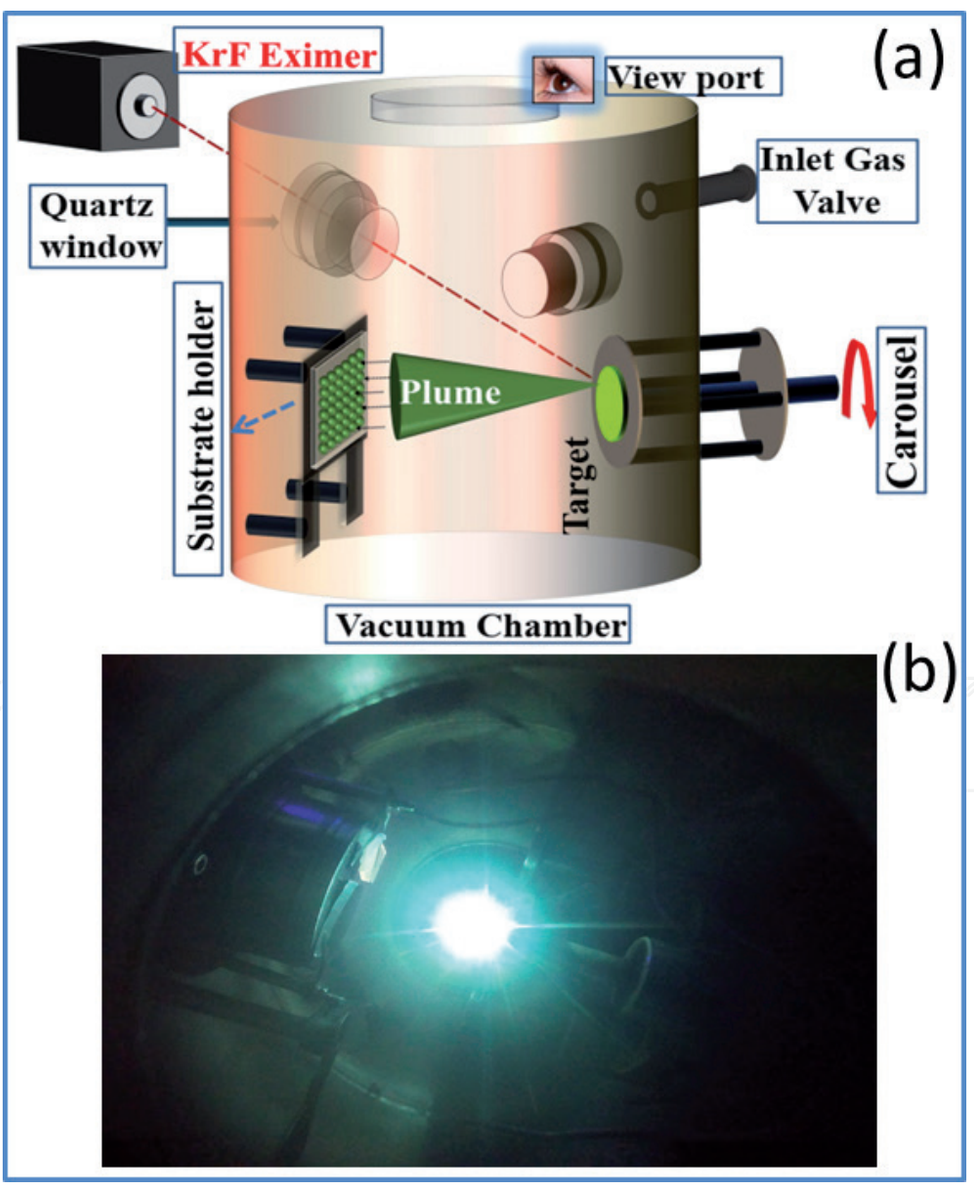

Figure 10.
(a) Schematic diagram of PLD coating unit; (b) photographical image representation for "laser plume" at CSIR-CECRI India (Reprinted with permission from Ref. [28]. Copyright 2020 Royal Society of Chemistry).

Process parameters	Range
Laser Excimer energy	100–700 mJ
Pulse rate	1–50 Hz
In-situ Temperature	RT –700°C
Partial pressure	10^{-6}, 10^{-4}, 10^{-2}
Inlet gases	Ar, N_2, O_2
Distance between target and substrate holder	5 cm
Vacuum pressure	1×10^{-7} mbar
Target size	1–2 inches

Table 2.
Thin film fabrication process parameters in pulsed laser deposition (PLD).

target of the materials in a high vacuum pressure up to 10^{-7} mbar with the help of turbo molecular pump. The laser excimer emits the laser pulse energy 0.8 joule/ pulse at a wavelength 248 nm uses high power (40 W) laser pulses to melt, and evaporate and ionize material from the surface of a target. This laser ablation event produces a high plasma plume that magnify intensely ahead of the target surface, and the produced laser plume is shown in **Figure 10b**. Additionally, PLD unit having rotating target carousel is used to make larger composite materials film in an ambient vacuum condition. PLD is used to fabricate all metals (Au, Pt, Ni, Ag, Cu, Al, etc.), metal oxides (MnO_2, V_2O_5, Co_3O_4, NiO, SnO_2 etc.), metal sulfides (MoS_2, CoS, NiS, FeS and VS_2 etc.), metal nitrides (CrN, TiN, VN and BN), conducting polymers (PANI, PPy etc.), solid state polymers (LIPON etc.) and other metalloid compound thin films for countless applications. While PLD is the stoichiometric conversion of the ablated material on or after the target directed to the substrates and the crystallite phase of the subsequent film is not essentially the similar that the target of materials.

From these consequences PLD is one of the ideal candidates to form micro / Nano structured films for energy storage and energy saving applications. Recently, de Krol et al. fabricated $BiVO_4$ thin film prepared by PLD for solar water splitting application [51]. Wang et al. investigated supercapacitor performances of NiSe thin film electrodes fabricated by PLD technique and the corresponding electrodes delivered specific capacitance value 696 F g^{-1} [52]. Patil et.al studied effect of temperature of $CoFe_2O_4$ thin film prepared via PLD for supercapacitor studies [53]. This work $CoFe_2O$ thin film annealed at 450°C electrode exhibited 777 F g^{-1}. Julien et al. examined Li_2TiO_3 thin film electrodes produced by PLD aimed at energy storage application. Here the LTO thin film grown at 600°C delivered a specific discharge capacity of 46 μAh cm^{-2} [54]. Lastly Author group demonstrated WO_3 and V_2O_5 symmetric thin film supercapacitors and Supercapbattery device assembled by using in-situ annealed thin film electrodes prepared by PLD. Thin flexible Supercapbattery device presented superior charge storage performance, also the device displayed high volumetric capacitance about 40 F cm^{-3} [28]. As a final point, PLD is the most appropriate technique for energy storage device fabrication.

1.4 Current electrode materials for thin film energy storage

Current commercial flexible energy storage system contains anode and cathode are regularly exclusive based on the intercalation/ deintercalation principal of potassium or lithium ions. Even though these flexible energy storage system by now exhibit a greatly upgraded when compared to the conventional supercapacitors of 10 years ago, their energy storage mechanism principle is also subject to essential limitations

prominent to comparably low energy storage system densities. One of the challenging application for supercapbatteries in terms of specific energy and power densities in future portable Micro-electronics. Transition metal oxides such as RuO_2, Fe_2O_3, Co_3O_4, WO_3, V_2O_5, NiO, Bi_2O_3 etc., and ternary metal oxides $NiCo_2O_4$, $ZnCo_2O_4$, $NiMoO_4$, $ZnWO_4$ etc., have long been disregarded as possible electrode materials for all kinds of energy storage system such as Lithium ion batteries, Supercapacitors and Supercapbatteries because of the they having high pore volume with high crystalline nature for insertion / deinsertion of electrolytic ions. The positive electrode as the cathode, the positive electrode frequently has a superior potential than the negative electrode (Anode). The current always streams from the positive electrode to the negative electrode via the peripheral circuit, and the electrons movement in the opposite way. However, cathode (positive) and anode (negative) are well-defined, by the electrochemical electrode reaction being reduction or oxidation.

1.4.1 Anodic materials

For fabrication of hybrid energy storages such as ASCs and Supercapbatteries, anodic materials are promising candidate to meet future energy demands. Usually anodic materials charges stored through an electrolytic ions intercalation/ deintercalation mechanism. As a result, the rate capability performance of hybrid EES is restricted by the sluggish kinetics of ion diffusion in the solid surface, as the surface adsorption–desorption approaches at the cathodic materials are noticeably more rapidly than the Faradaic reactions occurs at the anode, More than a few materials, Bi_2O_3, MoO_3, Fe_2O_3, VN and WO_3 are being investigated as the suitable anodes to fabricate hybrid EES because they are having high theoretical specific capacity, faster ions diffusion and easily allowing to intercalation of electrolytic ions.

1.4.1.1 Tungsten trioxide (WO_3)

Tungsten trioxide (WO_3) is a noticeable anodic material for the intention that of its low-cost and rich oxidation states (W^{4+}, W^{5+}, W^{6+}); WO_3 has in modern times become visible as an apparent anodic electrode material in the development of pseudo-capacitive nature due to its exceptional electrochemical performance and global profusion [55, 56]. However, even though WO_3 has well-known its potential as a proficient candidate for a widespread mixture of applications, it's an ideal applicant for thin film EES applications; the active material ought to contain high conducting nature and be capable to providing extraordinary electrochemical performance. Very few of reports on its presentation as an anodic active material in the assembly of a SC in addition to battery necessitate to further investigation in this pathway [57]. Recently author effectively achieved WO_3 Nano structure decorated (**Figure 11a**) on the surface of thin films, grown in an in-situ annealed condition by using well established PLD coating unit. Furthermore High resolution transmission electron microscopy (HRTEM) investigation using the WO_3 Nano particles with the morphology shown in **Figure 11b** in addition that the elemental distribution analyzes of W and O the color mapping images are shown in **Figure 11** c and d. From this contest author revealed that WO_3 is the one of the opted anodic material for TFSC device fabrications.

1.4.2 Cathodic materials

Usually, TMOs such as Co_3O_4, MnO_2, NiO, ZnO, V_2O_5, etc. are redox-active behavior and have been used as positive electrode materials for thin flexible energy storage.Most of the TMOs having good electronic conductivity, chemically stable, high theoretical specific capacities, low prices, abundance, and eco-friendly.

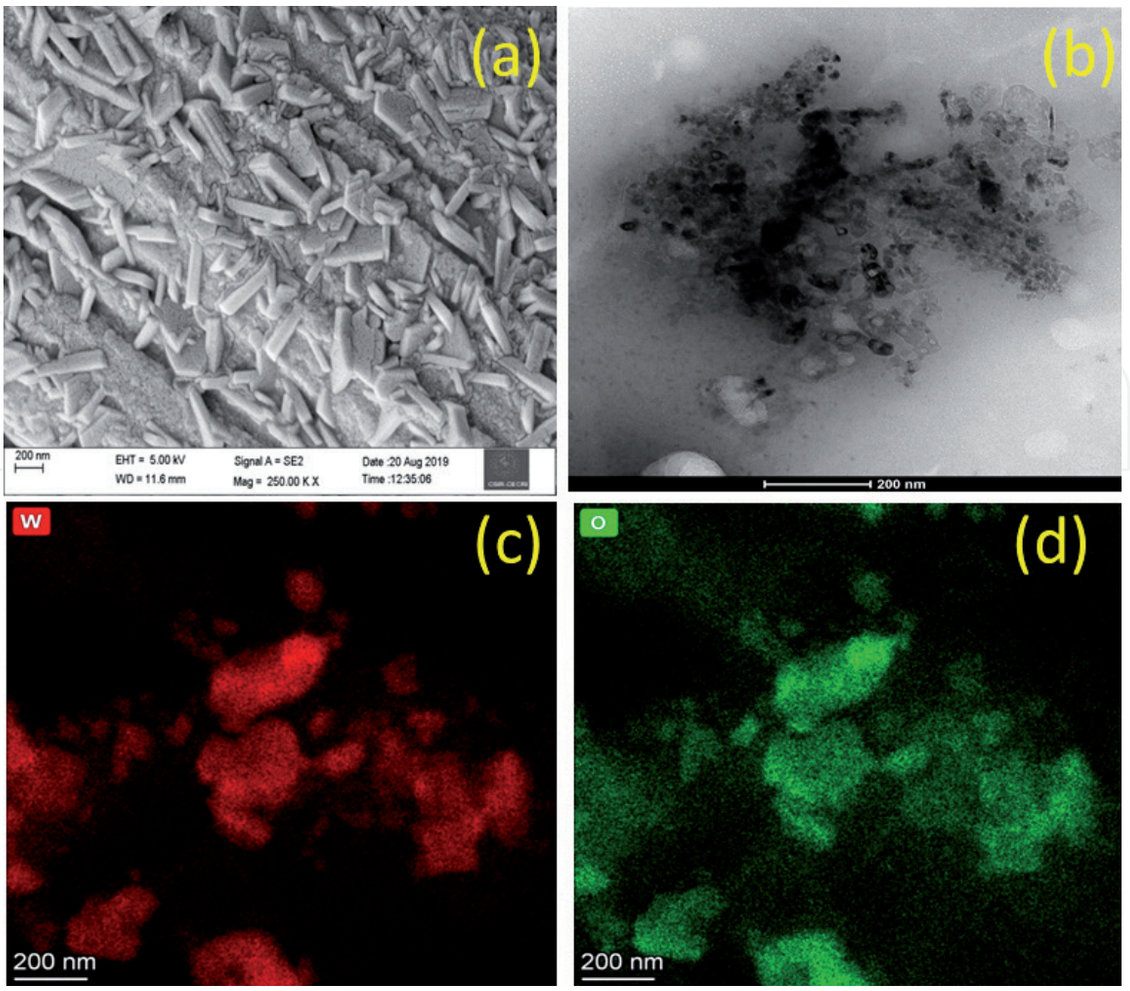

Figure 11.
(a) FESEM morphology of WO_3 Nano structures; (b) HRTEM Nano particles image; (c, d) HRTEM- EDAX color mapping images of W and O (Reprinted with permission from Ref. [28]. Copyright 2020 Royal Society of Chemistry).

1.4.2.1 Vanadium pentoxide (V_2O_5)

Vanadium pentoxide (V_2O_5) is a well-known electrode active material for EES applications in the middle of vanadium family as stated by Whittingham et., Vanadium pentoxide has variable oxidation states (V^{5+}, V^{4+}, V^{3+}, and V^{2+}), permitting it to attain high capacity than the other TMOs and layered structure of V_2O_5 creates it highly striking for EES applications. [58, 59] V_2O_5 has also paying attention as an active material for improved green EES systems. V_2O_5 with diverse morphologies in an adequate particles and thin film Nano structures have been fabricated by a variety of methods. In particularly physical vapor deposition (PVD) techniques are promising tool for thin film Nano structure fabrication. Recently author fabricated V_2O_5 thin films by using thermal evaporation technique with different thicknesses such as 210 nm, 380 nm, and 540 nm respectively [46]. As fabricated films further gone to symmetric SC device assembly, further all devices subjected to investigate electrochemical studies. The thin film thickness of 540 nm (cross section **Figure 12b**) symmetric device showed better electrochemical performance as clearly indicated from CV curve shown in **Figure 12a**. Meanwhile, thin film electrodes annealed at 500°C showed redox active behavior than as-prepared film (**Figure 12c**). The post annealing condition is also important for SC device performance because the annealed film morphology (**Figure 12d**) clearly shows the larger grain size.

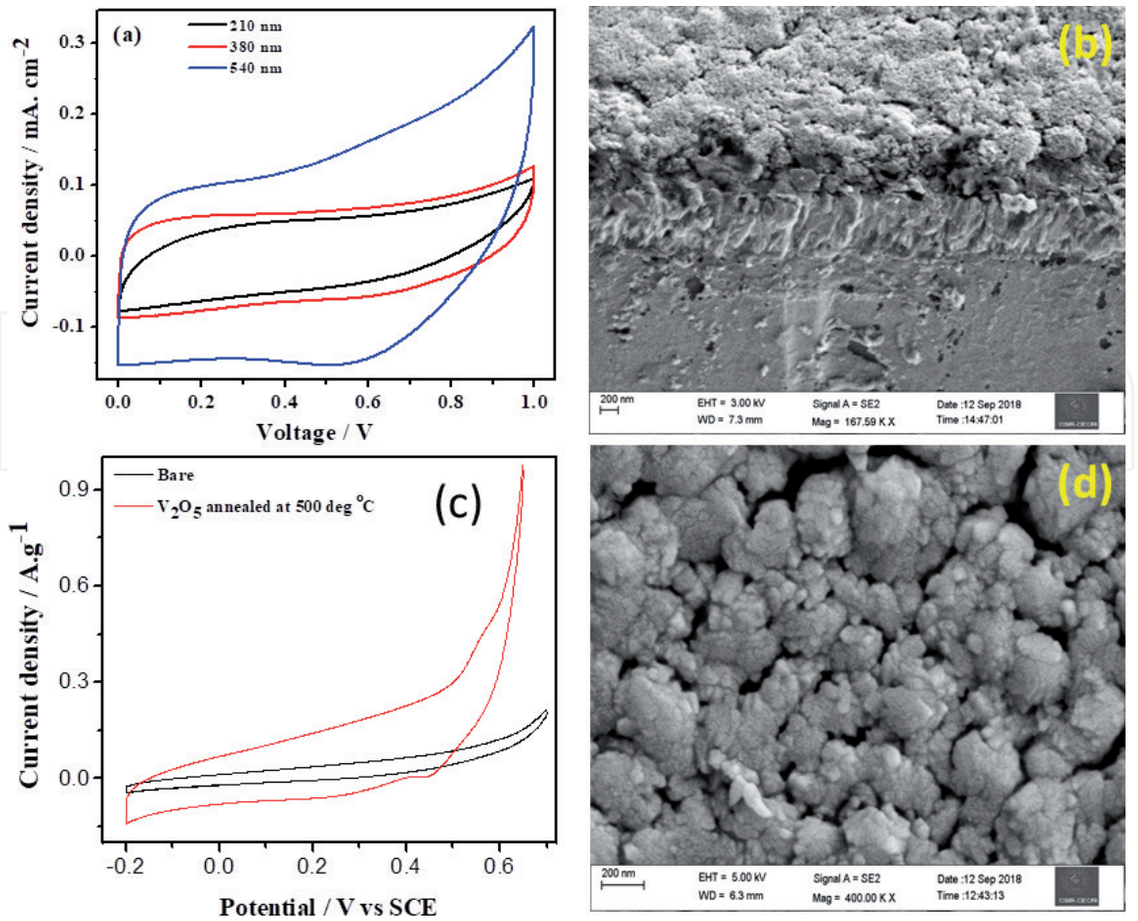

Figure 12.
(a) CV curve comparison of V_2O_5 symmetric capacitors in different thicknesses; (b) FESEM cross sectional image of V_2O_5 thin film fabricated by thermal evaporation coating unit; (c) CV curve comparison of bare substrate and V_2O_5 thin film annealed at 500 °C in a three electrode configuration; (d) FESEM morphology of V_2O_5 thin film annealed at 500 °C (Reprinted with permission from Ref. [46]. Copyright 2019 American Chemical Society).

In thermal evaporation technique, have some draw backs such as large molten materials are required for film fabrication. To overcome this issue author reported V_2O_5 thin film electrode fabrication by using PLD. PLD has some unique features such as layer by layer coatings, in-situ annealing condition, fine thickness control and inlet gases atmosphere while film fabrication. The author lastly reported work V_2O_5 Nano rods (**Figure 13a**) grown on flexible thin substrate with the help of PLD in an in-situ annealed 500°C at partial pressure atmospheric condition [28]. Further, the Nano structure investigation by using HRTEM is well agreed with Field Emission Scanning Electron Microscope (FESEM) morphology as displayed in **Figure 13b**, also the elemental distribution of vanadium and oxygen was uniformly distributed as presented in **Figure 13c** and **d**.

1.5 Flexible electrodes for thin film energy storage

As yet, it is still foremost contest to fabricate flexible thin electrodes with robustness mechanical belongings and outstanding electrochemical performance. The TFSC device fabrication current collector must be an essential tool to supply power to the active materials. Normally, conducting metal foils are used as substrates or electrodes for EEs devices [7, 60]. In particularly, TFSC device manufacture flexible current collectors can be needed; at the present time EES device fabrication usually used flexible electrodes such as 2 dimensional metal foils (Ti foil, Ni foil,

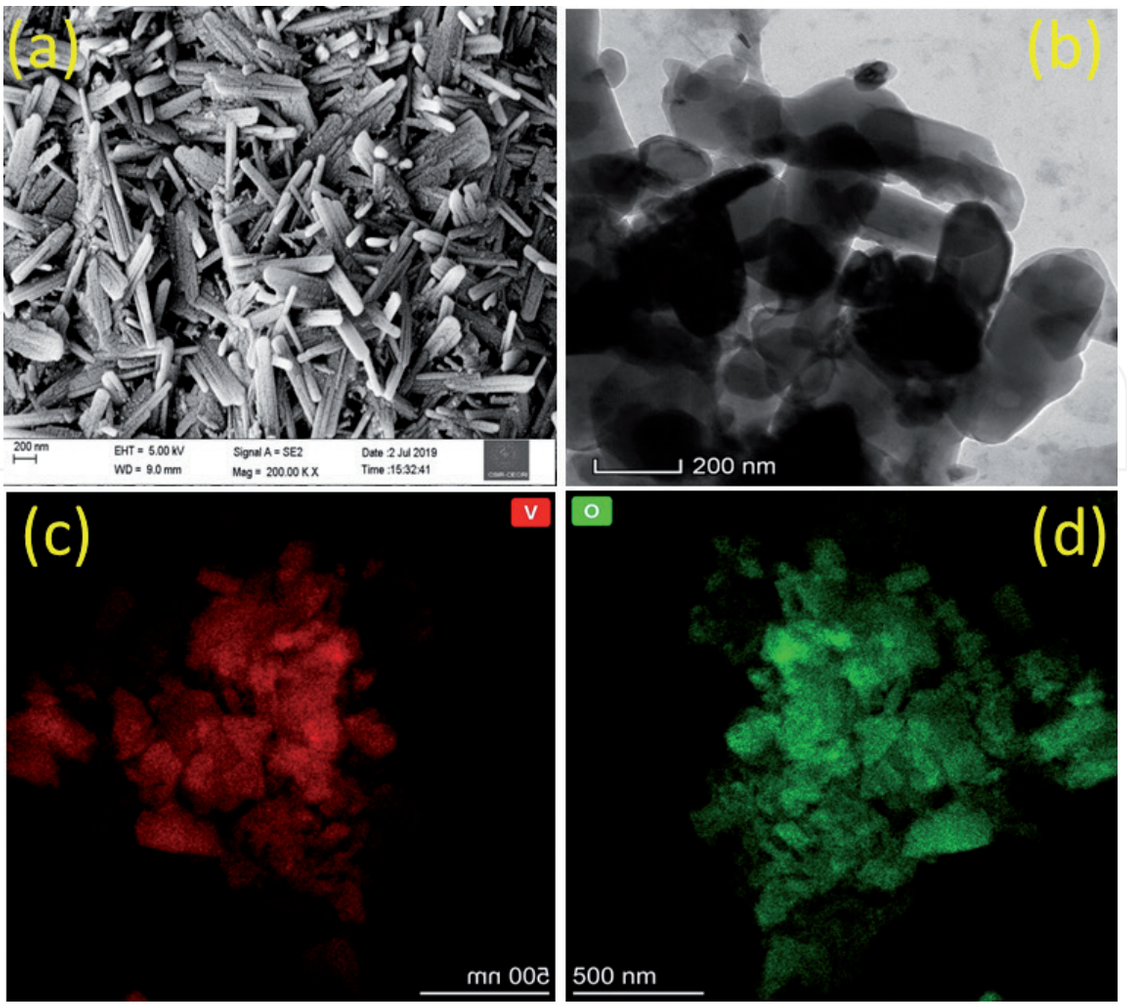

Figure 13.
(a) FESEM morphological image of V_2O_5 thin film Nano rods grown by in-situ annealed at 500°C in a partial pressure atmosphere; (b) HRTEM Nano particle morphological image of V_2O_5 Nano rods; (c and d) HRTEM-EDAX color mapping images of V and O (Reprinted with permission from Ref. [28]. Copyright 2020 Royal Society of Chemistry).

and stainless steel foil), conducting carbon clothes, and 3 dimensional arrays (Ni foam, cu foam, and graphite foam) have been widely used for the deposition of a combination of capacitive materials, conducting additives and binder. Nevertheless, metal foils are definitely corroded in aqueous electrolytes, which limits the lifetime of the devices [7, 30]. As a result, foregoing efforts have been attentive on the device design and fabrication of TFSC electrodes by way of non-metal materials. Even though, author used carbon paper substrates in aqueous electrolyte while fabrication of TFSC device used flexible Ni foam array is shown in **Figure 14a** and as prepared TFSC device shown in **Figure 14b**. In set **Figure 14b** clearly indicates Ni foam is one of suitable conducting flexible electrode for TFSC device manufacturing.

1.6 Electrolyte for thin film energy storage

The solid-state electrolyte is one of significant key components for fabrication of flexible TFSCs. In assessment to aqueous electrolytes, solid-state electrolytes are at ease to handle, and have superior reliability and an extensive range of working temperature. In addition, with a solid-state electrolyte can avoid a leakage issue, and consequently, which is reducing the device packaging cost [61]. The most extensively used solid-state electrolytes in TFSCs are gel polymeric mixture. A good solid state electrolyte is a non-toxic material, fabrication cost is low and with high ionic conducting nature, excellent stability, functioning at ambient temperature,

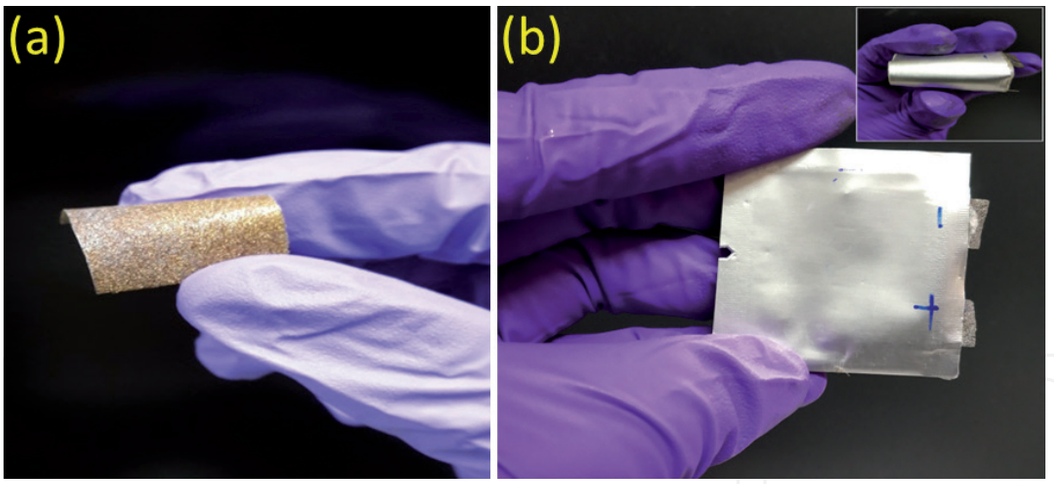

Figure 14.
Photographical image representation at CSIR-CECRI, India (a) V_2O_5 thin film deposited on Ni foam substrate; (b) author group fabricated thin film device.

better mechanical strength and an extensive potential window. In comparison gel polymer electrolytes exhibit superior ionic conductivity than dry solid-polymer electrolytes further down ambient conditions. Gel polymer electrolytes classically contains in a polymeric mixture as the host of an aqueous / organic solvent used as the plasticizer, and a secondary electrolytic salt. Poly ethylene oxide (PEO), poly vinyl alcohol (PVA), polyacrylonitrile (PAN) and poly (methyl methacrylate) (PMMA) are the maximum frequently used for preparing polymeric gel electrolyte mixtures. Author group reported fabrication of TFSC and Supercapbattery devices solid state PVA-KOH gel polymeric mixture was used [28, 46].

1.7 Significant parameters for estimating the device performance of flexible energy storage device

There are two significant parameters for estimating performance of Flexible energy storage devices such as volumetric energy density and volumetric power density of a TFSC device can be evaluated by using Eqs. (1) and (2)

$$E = \frac{1}{2}\frac{C_{cell}V^2}{3600}\left(\frac{mWh}{cm^3}\right) \tag{1}$$

$$P = \frac{E}{\Delta t_d} \times 3600\left(\frac{mW}{cm^3}\right) \tag{2}$$

Where C_{cell} is the specific capacitance of the TFSC device, V is the device working voltage and Δt_d is the discharge time. Based on Eq. (1), to achieve high volumetric specific energy density and volumetric specific power density, there is a necessity to rise C and V even though reducing R_s. Make best use of the TFSC device specific capacitance and voltage window are straight approaches to magnify the volumetric energy density of TFSCs. The working voltage window is determined by the electrode active materials and electrolytes.

The dynamics of thin film solid state battery as well as Supercapbattery devices for estimating specific volumetric capacity from discharge rate performance can be evaluated by using Eq. (3)

$$C_v = \frac{i\Delta t}{3600\, v}\left(\frac{mAh}{cm^3}\right) \tag{3}$$

Where C_v is specific volumetric capacity of the supercapbattery device. υ is the volume of the thin film supercapbattery device and Δt is the discharge time. Author group reported the thin film supercapbattery device showed excellent rate performance and the device delivered maximum volumetric discharge capacity ~32 mAh cm^{-3} at a current density of 1.3 A cm^{-3} [28]. This is unique instance for thin film supercapbattery energy storage was stated via PLD system.

To investigate essentially meaningful volumetric energy and volumetric power densities of a TFSC device, it must be fabricated and examined as a widespread sized and enveloped device. The essential calculation of volumetric energy and volumetric power densities ought to be based on the total area as well as volume of the whole device together with the thin film electrodes, solid-state gel electrolyte, the separator, current collectors and wrapping materials. Author reported supercapbattery device delivered maximum volumetric energy density about 12.5mWh cm^{-3} is displayed in **Figure 15**. Furthermore, the thin film Supercapbattery device delivered the steady performance of cycle stability even if an assorted bending position is shown in **Figure 16a**. Finally, the flexible TFSC tested the practical viability by illuminating Blue Light Emitting Diode (LED) glow (**Figure 16b**) with the series combination thin film devices, TFSCs well thought-out to be probable candidates for use in biomedical and wearable Microelectronic applications.

1.8 Reaction kinetic mechanism

The supercapbattery device showed fast kinetics with good storage behavior. The investigated results are extremely specific and exciting in terms of stability, volumetric energy and power density. This development in the supercapbattery device characteristics are essentially attributed to the electrode fabrication where the PLD

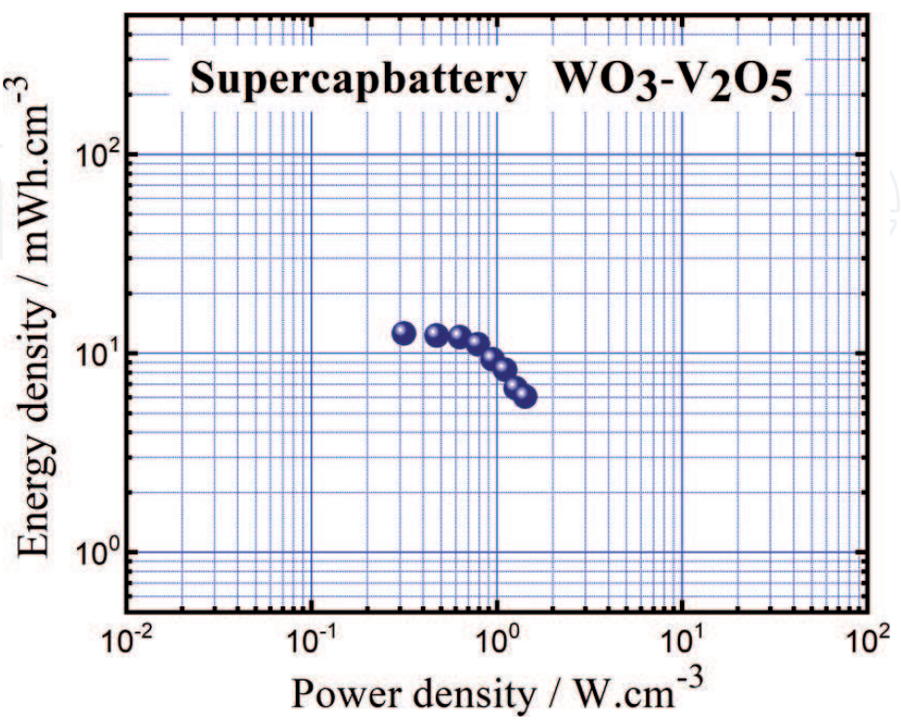

Figure 15.
Ragone plot for thin film supercapbattery device.

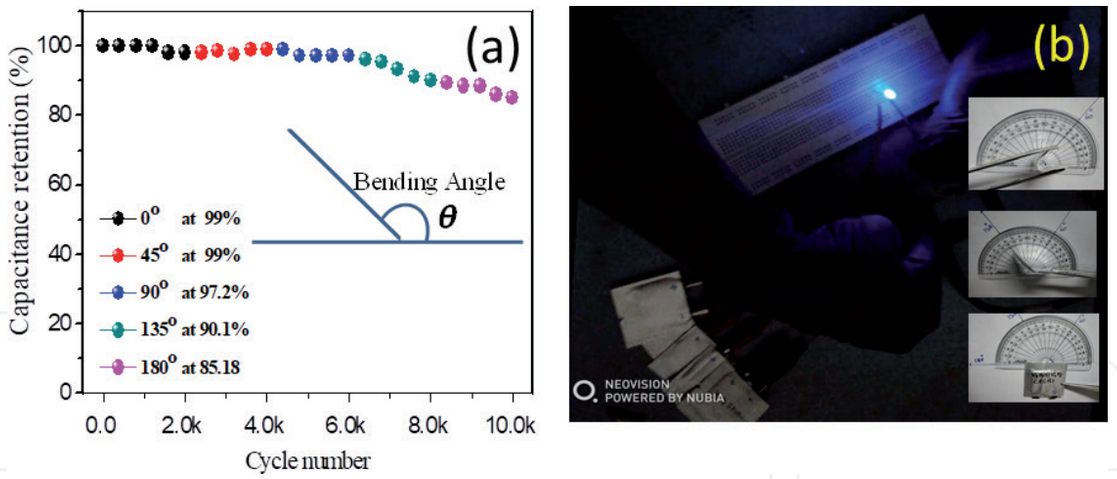

Figure 16.
(a) Stability analysis of supercapbattery for different bent position; (b) photographic image representation for blue LED glow at CSIR-CECRI India (Reprinted with permission from Ref. [46]. Copyright 2019 American Chemical Society).

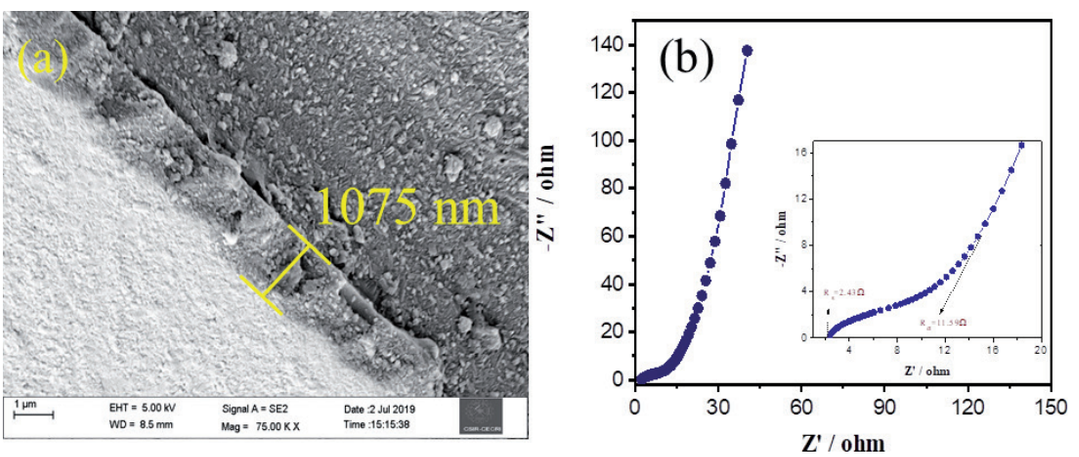

Figure 17.
(a) FESEM cross sectional image for V_2O_5 thin film fabricated by PLD; (b) EIS spectra for as fabricated supercapbattery device (Reprinted with permission from Ref. [28]. Copyright 2020 Royal Society of Chemistry).

deposition process plays an important role in such a Micro/ Nano scale devices. In order to make such supercapbattery device, the charge and mass balancing is very much important to construct, however, it is challenging to balance the charge 100% in practical devices. Instantaneously, in thin film energy storage, balancing of the charge storage can be attained easily by controlling the film fabrication process with the help of advanced coating system. Author's present study, the mass of the thin film electrodes was optimized using the characteristics observed from the three electrode system. On other hand optimized thickness of thin film electrodes are playing very important role for device fabrication, here in author group fabricated thin film electrodes separately with the help of PLD and the thicknesses of WO_3 and V_2O_5 thin film electrodes such as 1473 nm and 1075 nm is displayed in **Figure 17a**. Further this work reported total thickness of thin film supercapbattery device was 2.5 microns, even if the device presenting good conducting nature, Electrochemical Impedance Spectroscopy (EIS) is the best way to determining Resistance of any electrode or device. The thin film supercapbattery device showed very low charge transfer resistances R_{ct} value 11.9 ohms it's clearly indicating EIS spectra is displayed in **Figure 17b**. Thus the supercapbattery device delivered better electrochemical performances.

1.9 Future scope

Nano scale level thin film active materials brought significant improvement for the development of flexible thin film energy storage, Nano complex materials in the form of thin film facilitate accessible of electrolytic ions and an enhance the device rate capability. Nevertheless, an additional side reaction affected by increasing pore area must be taken into consideration for practical wearable and portable electronics. The flexible storage approach to combine in the form of thin film energy storage advantages of different active materials is a hopeful approach for forthcoming development.

Gradually thin film based composite energy storages demands have led to necessities for more specific functions in an electrochemical energy storage devices. Furthermore, outdated Supercapbatteries are undertaking modernizations in different directions to encounter the special necessities of modern society. Here, promising development ways for Supercapbatteries for future as follows

- Microchip energy storage; Easy handling and wearable electronic apparatus is progressively becoming an essential in ordinary life, resulting in the perseverance to improve highly-integrated, diminished and Nano/ Micro-sized energy storage devices. Here, the gradually thin film composite necessities of Nano / micro- scale devices such as smart phones with intellectual operations will necessitate the expansion of materials on the atomic scale in the predictable future

- Portable and self-charging energy storage; Flexible thin wearable and stretchable energy storage devices are foreseeable trend in the imminent development of electrical devices for energy transports, drug delivery, recyclable testing, lighting apparatus, communication equipment's and sensors as well as other applications in which the features of next generation portable products to enable direct wearing or direct connection to skin necessitate thin electrode materials with exceptional flexible, high deformation and low toxicity.

- Implantable energy storage devices; The fast progression of biomedicine and human health witnessing has led to promising demands for implantable very thin energy storage devices to permit for bioinformatics assembly, real-time pathological detection, active drug delivery and clinical usages in which the immeasurable mechanical and kinetic energy from the bio body (e.g. breathing, workout, blood circulation, and heartbeat) can fulfill the self-supply of energy to implantable energy storage devices.

2. Conclusion

This chapter converses several properties of thin film influencing their electrochemical performance such as cyclability, energy and power density and so on. Author have performed the comparison studies of two class of energy storage mechanism between supercapacitor and supercapbatteries have been considered to improve large potential window in solid state electrolyte as well as aqueous electrolytes. Flexible thin film supercapbatteries employing with the help of PLD system are expected to exhibit good electrochemical redox activity to deliver high voltage window yet showing a better stability in a post annealed temperature conditions. The thin film supercapbatteries consisting of Tungsten trioxide and vanadium pentoxide has to be a potentially interesting flexible thin film based device, that is simple, low cost, portable and eco friendly. There are no draw backs as the electrode

materials because the fabricated electrode materials delivered better cycling stability in a different bent position and both materials having good electrical conductivity. Thus, WO_3 and V_2O_5 thin film electrodes are promising candidate for flexible thin film energy storage applications and numbers of surveys are highly acceptable to discover the potential of these thin film energy storage materials with highly adhesive film fabrication methods.

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List of symbols

R_s	Solution resistance (Ω)
R_{ct}	charge transfer resistance (Ω)
Δt_d	discharge time(s)
E_v	Volumetric specific energy (mWh cm^{-3})
P_v	Volumetric specific power (mW cm^{-3})
E_a	Areal energy density (μWh cm^{-2})
P_a	Areal power density (μW cm^{-2})
C_s	Specific capacitance (Fg^{-1})
C_a	Areal capacitance (mF cm^{-2})
C_{cell}	Volumetric capacitance (F cm^{-3})
V	Voltage window (V)
C_g	Specific capacity (mAh g^{-1})
C_V	Specific volumetric capacity (mAh cm^{-3})

Acronyms and abbreviations

PVD	Physical Vapor Deposition
PLD	Pulsed Laser deposition
EES	Electrochemical Energy Storage
ED	Electrochemical deposition
CVD	Chemical Vapor Deposition
ALD	Atomic Layer Deposition
ESDs	Energy storage devices
SCs	Supercapacitors
LIBs	Lithium Ion Batteries
TFSCs	Thin film supercapacitors
AFM	Atomic Force Microscopy
RT	Room temperature
CV	Cyclic Voltammogram
GCD	Galvanostatic Charge and Discharge
ASCs	Asymmetric supercapacitors
SSB	Solid state batteries
TMOs	Transition Metal Oxides
V_2O_5	Vanadium pentoxide

WO_3	Tungsten trioxide
KrF	Krypton Florine
FESEM	Field Emission Scanning Electron Microscope
HRTEM	High resolution transmission electron microscopy
PEO	Poly ethylene oxide
PVA	Poly vinyl alcohol
PAN	Polyacrylonitrile
EIS	Electrochemical Impedance Spectroscopy
LED	Light Emitting Diode
CSIR	Council of Scientific & Industrial Research
CECRI	Central Electrochemical Research Institute

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