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Multi-responsive Supercapacitors: Smart solution to store electrical energy

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With increasing demand for economic and eco-friendly energy conversion and storage system, smart devices integrating both energy conversion and storage have received increasing attention as a key breakthrough for efficient energy utilization. In recent years, significant attempts are made in the integration of the two technologies taking all possible means into account to convert energy efficiently. Among the options, multi-responsive supercapacitors which can be charged using diverse renewable resources, e.g. mechanical force, temperature or light, are widely considered as a promising energy integrated system because of the unique characteristics of supercapacitors, such as fast charging/discharging rate, high power density, simple configuration. In this review, we provide insights into the mechanism of converting mechanical force, temperature and light into electrochemical energy. We shed light on various alternatives to store electrical energy using an electrochemical energy storage unit to realize multi-responsive supercapacitors. In addition, other means of enabling electrochemical energy storage are also discussed in brief. The challenges of the integrated system for simultaneous realization of energy conversion and storage are highlighted.

Key words: multi-responsive supercapacitor, piezoelectric conversion, triboelectric conversion, electrochemical energy

1. Introduction

The ever increasing demand of energy has propelled the level of greenhouse gases and air pollutants (in particular, fine particles) in the environment[1]. To mitigate adverse changes in the climate or eco-system, massive efforts are in progress to develop clean and green energy production and storage technologies, which can provide sustainable and eco-friendly solutions to meet the end users requirements. Wind energy or solar energy is known to be the leading renewable energy technology so far after hydro power, and contributes about 2.3% or 0.98% in the global energy production, and their role now has become obvious in various applications, for instance, powering up buildings, and pumping water[2]. As the renewable energy sources are integrated into the grids, the understanding on the effect of their intermittent nature is attracting more attention, as it triggers the mismatch between supply and demand[3]. The conventional energy storage technologies, typically batteries, are not capable to cope in these circumstances, as they could not charge/discharge quickly. This mismatch creates “use it or lose it” condition. To address this discrepancy, a smart energy storage technology is required that can charge and discharge in such a way, so that the output will not be affected by the external factors. Supercapacitors are known for their fast charging/discharging rate, power density, and ultra-long calendar life[4]. They are used in power equalization systems, such as wind power applications to provide uninterrupted power distribution at the time of wind gusts or deep wind fluctuations [3]. The second largest supercapacitor market comes from the automotive applications[5]. Undoubtedly, batteries are the promising energy sources for electric vehicles due to their high energy density, but batteries do not meet the high power requirements (while accelerating and climbing) due to their low power density[6]. On the other hand, supercapacitors possess high power density and they can be charged quickly, therefore, regenerative braking is possible[7]. It is found that by combining supercapacitors with the batteries, effective life time of batteries can be improved as well as consumption of fuel can be reduced about 15%[8].The integration of smart energy storage technologies, i.e., supercapacitors, with the renewable energy production and storage, is a leading strategy where the energy can be effectively utilized[9].

Supercapacitor consists of positive electrode and negative electrode separated by a conventional separator film (e.g., filter paper) and immerse into an electrolyte solution[4]. Supercapacitor (electric-double-layer capacitor) is associated with the potential dependent accumulation of the

charges (deficit or excess of conduction band electrons) at the electrode surface, and to establish the charge neutrality electrolyte ions with counter balancing charge built up on the electrolyte side. During charging process, electrons travel from negative electrode to positive electrode due to external load, while cations in the electrolyte move towards negative electrode and anions move towards positive electrode. Thus, an inner Helmholtz plane or electric double layers capacitor (EDLC) configuration develops, and stores energy in the form of electric charges. However, the formation of outer Helmholtz plane as well as diffuse layer (solvated cations) also takes place, but barely partakes to store charges. It has to be noted that there is no net charge (electronic or ionic) transfer across the electrode/electrolyte interface. This entails that the concentration of electrolyte ions remain fixed during the charging and discharging process. In contrast to the conventional understanding about the charge storage in electric-double-layer capacitor, it is also identified that the charge storage occurs at the electrode/electrolyte interface as well as within the electrolyte[10]. The charge stored at the interface takes only a few seconds, while the charge stored in the electrolyte takes hundreds of seconds. It is also identified that the performance of charge storage can be affected by the nature of oxygen ions present on the surface of the electrode[11].

In contrast to the batteries where working voltage is constant, the voltage in supercapacitors is proportional to the amount of stored charge. The maximum charging voltage of supercapacitor is the voltage at which the supercapacitor is fully charged. The maximum charging voltage can be determined on the basis of the capacitive potential range of positive and negative electrodes[12–14]. For symmetric device configuration, the device voltage is equal to zero, in fully discharged state of the device, this state is known as the point of zero voltage (open circuit potential). In case of asymmetric device configuration, the device voltage is not equal to zero in its fully discharge state or the maximum charging voltage has to take into account the point of zero voltage in order to fully charge the device[12]. Therefore, the state of the chargeable voltage of supercapacitor is an indication whether the device can be integrated with the other functional unit or not.

It is widely accepted that the inherent electrode properties are the major limiting factor in the integration of supercapacitor devices with the other energy-converting or –storing units[15]. Although some of the electrode materials with small open circuit potential are capable in satisfying the requirements to be integrated[16], however, those integrated supercapacitor units

require switching of the circuit connections in the process of charging/discharging. Therefore, a stand-alone multifunctional supercapacitor is highly desirable that can store energy without the need of reconnections. Recently, it is demonstrated that the supercapacitor device can be charged by unconventional means[17–20], in other words, electrical energy can be stored in supercapacitor by the means of pressure/temperature/light etc, as depicted in Fig.1. For example, the electrochemical energy storing unit can be charged under compression, i.e., mechanical force, in which ions are driven by piezoelectric field rather external electric field. During mechanical energy harvesting or piezoelectric driven charging of supercapacitor, the frequency at which the mechanical force is exerted plays a vital role on the efficiency of charging process. For instance, the efficiency of supercapacitor is lower during the initial charging stages at lower frequencies, and reaches a nominal voltage at higher frequencies[21]. Not only physical but also biological processes can also lead to charging the supercapacitor unit, for example, oxidation and reduction of enzymes (Myrothecium verrucaria bilirubin oxidase and Corynascus thermophilus cellobiose dehydrogenase) in the carbohydrate/oxygen enzymatic fuel cell can provide a constant open circuit potential of 400 mV at a current density of 50 mA/g[22]. Moreover, illumination under sunlight has also been utilized to power up a supercapacitor device[23,24]. The charging time to reach at a nominal voltage of V_x can be determined by taking capacitance (C_{sp}) of supercapacitor and short circuit current (I_{SC}) of the device into account. In addition to light illumination, a supercapacitor can be charged thermally, as the kinetics of Faradaic reactions can be altered by thermo-electrochemical processes[25–27].

Figure.1. Functional characteristics of supercapacitor integrated with other energy conversion technologies

In this review articles, we provide a brief summary of recent research progress on the unconventional means of charging an electrochemical energy storage unit (supercapacitor), which includes piezoelectric, triboelectric, light, temperature (heat) assisted charge storage. Other unconventional means to charge a supercapacitor are also discussed.

2. Charging of supercapacitor by mechanical force (triboelectric)

Among various means of converting or harvesting mechanical energy, triboelectric nanogenerator device is attracting enormous attention due to its ease of operation and high output voltage[28,29]. The working principle of triboelectric nanogenerator is based on contact and separation induced electrification and electrostatic induction[30]. These types of nanogenerators utilize the most common form of the materials and convert almost all types of mechanical energy, such as rain drop, bending, sliding, vibration, water wave, air flow, rotation, etc.[31] into electricity. A triboelectric driven multi-responsive cell can be constructed with three components, namely, energy harvesting unit, rectifier, and an energy storing unit.

Recently, a simple and cost efficient method to fabricate a multifunctional cell with a supercapacitor unit and triboelectric unit is introduced. The as-developed multifunctional cell was able to charge up to 3V under pressing or bending, and showed an exceptional electrochemical stability under mechanical forces[32]. The maximum charge density that could be transferred by triboelectric nanogenerator was about $68 \mu\text{C}/\text{m}^2$, with a peak power density of $0.8\text{W}/\text{m}^2$. In fully charged state of the cell, it could light-up two LEDs or a panel of commercial humidity sensor. The device structure is schematically illustrated in Fig.2a. To generate electrostatic charges during contact-separation, a PTFE (poly-tetraflouroethylene) film coated with PTFE nanoparticles was used, as depicted in the bottom of Fig.2a. Fig.2b depicts the FESEM micrograph of laser induced graphene (LIG) layers that were separated by a polyamide film. Supercapacitors were designed on graphene using a computer controlled laser system. The inset of Fig.2b clearly revealed the highly porous nature of LIG. Fig.2c-d presents topographical and micro-structural information about the LIG layers. In their demonstration, the individual unit, i.e., triboelectric nanogenerator and supercapacitor was tested separately, and found that each unit could achieve high performance.

Figure.2. (a) Schematic illustration of the design of multifunctional cell, top inset is the digital image of the cell, and bottom inset is the SEM micrograph of PTFE nanopatrics, (b) cross-sectional SEM of the cell, (c) SEM image of laser scribed graphene, inset is the magnified view, and (d) HRTEM micrograph of graphene. Reprinted with permission from ref.[32] copyright@2015, Tsinghua University Press and Springer-Verlag Berlin Heidelberg

It must be noted that the output voltage of nanogenerator is in alternating current (AC), and it is known for a supercapacitor that only direct current (DC) components can be stored[33]. Therefore, to filter AC components from the output of nanogenerator a full wave bridge rectifier was used, as depicted in the circuit diagram of the unit, the inset of Fig.3a. The supercapacitor could be charged to 3V with the application of bending, and the stored energy was capable to light-up two LED units, Fig.3b. Moreover, the as-designed multifunctional energy unit could be retrofitted into the insole of a shoe, Fig.3c, demonstrating its high potential of integration. To further demonstrate the application of this multifunctional unit, panel of a commercial humidity sensor was lit-up, as shown in Fig.3d-f.

Figure.3. (a) charging of multifunctional cell, inset is the circuitry diagram in energy supply mode, (b) digital image of LEDs that were lit-up by multifunctional cell, (c) retrofitting of the cell into a shoe, (d-f) digital images of the humidity sensor driven by multifunctional cell.

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To further improve the mechanical stability of the multifunctional cell, all plastic configuration of multifunctional cell is recently introduced[34]. At a frequency of 8 Hz, the maximum output voltage of energy storing unit (i.e., supercapacitor) could reach to 1.5 V in 1.36 hours, and it took 1449 sec to discharge at a load current of 2 μ A. Moreover, energy storing unit could be charged to 40 mV even by human finger in just 30 sec. The charge transfer density of nanogenerator was found to be about 82 μ C/m². The schematic illustration of the integrated unit is shown in Fig.4. In triboelectric nanogenerator, a PTFE film was used as the charge transferring unit with cauliflower-like poly-pyrrole (cPpy) as the back electrode and hollow-horn like poly-pyrrole (hPpy) as the other triboelectric layer and the electrode as well. In energy storing unit, hPpy film was applied as both positive and negative electrodes, where, polyethylene (PE) film and H₃PO₄/PVA (poly-vinyl alcohol) gel was chosen as separator and electrolyte, respectively. To improve the voltage output, four energy storing units were connected in series.

Figure.4. Schematic illustration of the steps involved in the fabrication of multifunctional cell. Reproduced with permission from ref. [34], Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Fig.5a shows integration of the block diagrams of nanogenerator and supercapacitor units with a full wave rectifier. The output voltage of energy storing unit was increased by connecting them in series, as shown in Fig.5b. As can be seen in Fig.5c, the output voltage of the device was highly dependent on the frequency of applied force; a maximum of 26 mV could be achieved in just 60 sec, when the frequency of the force was 10 Hz. The force is applied for a period of 1.36 hours to reach the output voltage 1.5 V, and it took about 0.40 hours to discharge at a loading current of 2 μ A, as depicted in Fig.5d. The cell could also be charged by human finger from 0 mV to 42 mV in 30 sec, with an average current of 2.5 μ A, Fig.5e. From the practical application view point, the energy storing units were able to drive a calculator to execute a series of calculations constantly, (Fig.5f).

Figure.5. (a) Circuit diagram of multifunctional cell in energy supplying mode, (b) photograph of multifunctional cell connecting energy storing units in series, (c) charging of multifunctional cell at various applied frequencies, (d) charging and discharging profiles of multifunctional cell, (e) charging profile of multifunctional cell by the application of human finger, and (f) photograph of the calculator driven by multifunctional cell. Reproduced with permission from ref. [34], Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

More recently, Song et al. proposed a new device design in which carbon nanotubes (CNT) based paper electrodes were sandwiched between wrinkled poly-dimethylsiloxane (PDMS) electrodes as a multi-responsive cell[35]. The energy storing unit (i.e., supercapacitor, CNT electrodes) could be charged to 900 mV within 180 min by the application of a periodic

compressive stress, the stored energy was sufficient to drive a calculator. Besides an electric switch, the multifunctional cell was utilized to drive an electrochromic window. The proposed device design offered several obvious advantages in comparison with the earlier attempts[33,34], for example, 50% of the charging voltage could be achieved within few tens of min. However, these cells were likely susceptible to malfunction due to individual components.

Luo and coworkers designed an intelligent unlocking system to identify individual's identity using multi-responsive cells as the platform[36]. The cell consists of fluorinated propylene film on grid-like indium thin oxide mesh and 3D Au@MnO₂ nanocomposites as power generating and storing units, respectively. By simply tapping human finger the charging unit was able to be charged from 0 volts to 2.5 V within 6102 sec, and discharged in 1639 sec with an applied current of 1 μ A. Interestingly, the charging time of the cell strongly depends on the sliding speed of the finger, nature of sliding, and pressure induced by the finger, indicating the potential for identity tracking.

In the progress of multi-responsive wearable electronics, Pu et al. developed a full electronic textile that consists of three main units, namely, energy storage unit (yarn supercapacitor), mechanical energy harvesting unit (triboelectric nanogenerator) and electronic sensor[38], as depicted in Fig.6a.

Figure.6. (a) Illustration of the scheme of a multifunctional textile, it integrates energy storing unit (yarn supercapacitor), energy harvesting unit (triboelectric nanogenerator) and wearable electronics, (b) Digital image of a multifunctional textile woven with energy storing and harvesting units. The magnified view of the energy storing unit shows two black yarn supercapacitors, and (c) The voltage profile of multifunctional textile. Reproduced with permission from ref. [38], Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

A photograph of multi-responsive textile is depicted in Fig. 6b, enlarged view in the inset shows alignment of energy storing unit, i.e., yarn supercapacitors. The chargeable textile could be charged to 2.1 volts in 2009 sec by the continuous operation of a vibrator, and the textile took 811 sec to discharge by the application of a loading current of 1 μ A, as shown in Fig.6c. When the vibration frequency was increased to 10 Hz, the charging current could be shortened to 913 sec, followed by discharging of the unit in 808 sec. It must be noted that the charging performance of the cells can be further improved by matching the impedance of energy harvesting and energy storage unit, as the resistance of the energy harvesting unit is several orders of magnitude higher than that of the energy storing unit. Due to the flexibility and ease of sewing of both the yarn supercapacitors and the nanogenerator, this multi-responsive textile perhaps can be incorporated into complex and designer textiles for motion charging, however, massive efforts are still required to design flexible components, such as rectifier and impedance balancing circuit into the wearable electronic textiles.

Moreover, the output electric power of nanogenerator is irregular in magnitude and consists of discrete pulses; therefore, it is difficult to directly use this output to power-up electric devices. Thus, it is essential to combine this power source with an energy storage unit that can provide stable and durable output. To combine energy storing unit (typically a supercapacitor device) with the energy harvesting unit, various device designs have been proposed so far. However, in most of the designs energy harvesting and conversion devices are separate entity, which limits their widespread applications.

3. Charging of supercapacitor by mechanical force (piezoelectric)

It is shown that the nanoscale mechanical energy can be efficiently converted into electrical energy due to coupling between semiconducting and piezoelectric property of piezoelectric material (e.g., ZnO nanowires)[39]. In the previous attempts, it was considered that the integration of energy generation and storage technology is difficult and perhaps affects the efficiency due to loss of the energy across rectifier. However in the recent years as a result of intensive research, not only a facile integration but also an efficient device configuration can be achieved[40]. Among the various energy conversion and storage technologies, the conversion or harvesting of mechanical energy into electrochemical energy is gaining significant attentions. Such an integrated device structure that can be charged-up by mechanical deformation or environmental vibration, is paving a path for innovative approaches to multi-responsive electronic devices, as an example, small scale mechanical deformation (e.g., human touch ~ 1 N), biomechanical deformation [41,42], can be directly stored in an electrochemical energy storage device. The energy (mechanical deformation) can be stored in supercapacitor or battery, however, as much as safety and power density is concerned supercapacitors are chosen over batteries. A multi-responsive electrochemical energy storage unit can be developed by incorporating a functional material as a separator. Recently, it is identified that a piezoelectric material can be used effectively as a separator in an electrochemical energy storage unit. The piezoelectric nanogenerator relies on the change in the piezoelectric potential developed by external mechanical force in the piezoelectric material[21]. In contrary to the other mechanical energy harvesters, e.g., triboelectric nanogenerators (where a structural-gap is required to function), piezoelectric material as a separator helps to integrate the unit. The energy harvested by piezoelectric nanogenerator can be directly stored in an electrochemical energy storage unit without the need of rectifiers, as the output voltage is highly directional and does not reverse in the absence of applied force.

Xu and coworkers pioneered an innovative means to generate electrical energy from low-energy vibrations/disturbances/stimulation using piezoelectric material, i.e., lead zirconate-titanate (PZT)[43]. The as-designed nanowires based energy harvester or converter, was capable to charge eight commercial 22 μ F capacitor devices, and could reach 0.42 volts. Moreover, the as-stored energy in the capacitors could drive a laser diode during discharging process. The

schematic illustration of the piezoelectric potential in the nanowires based mechanical energy harvester device is presented in Fig.7a.

Figure.7. (a) Schematic illustration of nanowires based piezoelectric device and distribution of electric potential in the nanowires, (b) charging process of a capacitor, and (c) digital images of laser diode before and at the moment when connected with the capacitor. Reproduced with permission from ref.[43]. Copyright, 2010, Nature Publishing Group

To effectively utilize the energy harvested by the piezoelectric nano-generator, a commercial full-wave bridge rectifier coupled with the energy storage units was used. The whole charging process was recorded by examining the potential across a capacitor, as depicted in Fig.7b, and could reach to 0.42 volts after several thousands of cycles. It has to be noted that the power generated by this integrated cell could not drive continuous operation of the laser diode, Fig.7c, due to small charge storing capability of the storing unit. The storing capability or efficiency of the multifunctional device can be enhanced by eliminating the intermediate state, i.e., generation of electricity and storing in a capacitor. In other words, a single mechanical to electro-chemical process is much more efficient than the mechanical to electrical followed by electrical to electro-chemical process to charge an electrochemical cell.

Recently, a direct mechanical to electrochemical process is proposed by combining piezoelectric material with the electrochemical cell to harvest mechanical energy directly as electro-chemical energy with higher overall efficiency[44]. The designed multifunctional cell was unique in functions the ions in the cell are driven by piezoelectric field rather electrons, therefore, movement of the ions solely depends on the polarity of the piezoelectric field. It was identified that retrofitting of piezoelectric separator in the electrochemical cell does not affect the

electrochemistry of the cell. The potential of the cell was increased by ~ 75 mV in 240 sec under mechanical force of 2.3 Hz frequency. During discharge with a loading current of $1 \mu\text{A}$, the multifunctional cell could last for 130 sec.

Figure.8. Schematic illustration of the design of multifunctional electrochemical cell, Reprinted (adapted) with permission from ref.[44]. Copyright (2012) American Chemical Society

The schematic illustration of the design of multi-responsive cell is depicted in Fig.8, in which the characteristic properties of both electrochemical and piezoelectric processes are utilized. As can be seen in Fig.8, the device structure of electrochemical cell remains the same except the substitution of separator film by a poled PVDF film ($110 \mu\text{m}$). In the device design, the role of PVDF film was similar to the power supply in the conventional charging process of an electrochemical cell. The polarity of PVDF film was precisely controlled so that positive electrode of the cell, i.e., LiCoO_2 experienced a positive polarity and the other electrode faced negative polarity. The mechanism of charging of multifunctional cell is schematically illustrated in Fig.9a-c.

Figure.9. Illustration of the mechanism of multifunctional cell, (a) graphical illustration of the multifunctional cell in its thermodynamic equilibrium (b) state of the electrodes and ions in the cell under piezoelectric field, and (c) movement of Li ions when the piezoelectric field is removed. Reprinted (adapted) with permission from ref.[44]. Copyright (2012) American Chemical Society

After the successful demonstration of piezoelectric effect driven multifunctional cell, the next important step was to improve the performance of the cell for practical applications. The performance of multifunctional cell could be further improved by enhancing the characteristic features of piezoelectric separator by confining the piezoelectric field. Zhang et al. developed a piezoelectric separator by intermixing PZT nanoparticles in the PVDF scaffold, and able to increase the output voltage from 210 mV to 300 mV in 240 sec by the application of mechanical force of frequency of 1.5 Hz[45]. The multifunctional cell was discharged back to its original state in 37 sec under a constant loading current of 1 μ A. The improvement in the multifunctional performance of the cell was ascribed to the enhancement in the piezoelectric coefficient of the composite film (PVDF-PZT), amplification in the piezoelectric potential due to geometrical strain confinement, a higher piezoelectric potential due to smaller inter-pores distance. The fabrication of multi-responsive cell is schematically presented in Fig.10a-c. As shown in Fig.10c, LiCoO₂ composites and MWCNT are used as cathode and anode, respectively, to fabricate the multi-responsive cell. The mechanism of energy storage in this multi-responsive cell was found similar to the mechanism proposed previously by Xue et al. except the improved intensity of the piezoelectric potential that was intensified by the PZT nanoparticles.

Figure.10. Graphical illustration of the steps involved during fabrication of multifunctional cell, (a) illustration of the mixing of piezoelectric components, (b) fabrication of planner electrodes, and (c) graphical illustration of the device design. © IOP Publishing. Reproduced with permission [45], All rights reserved

By considering the fact that piezoelectric potential of PVDF film is solely accountable for charging of the cell, therefore, controlling the physical properties of PVDF film was considered a key direction to further optimize the performance of multifunctional cell. The performance of the multi-responsive cell was further improved by altering the porosity of the PVDF film[46]. It is known that the strain can be confined effectively in the porous structure, as a result the strain induced piezoelectric potential can be utilized more efficiently[47]. The output voltage was increased from 116 mV to 298 mV in 250 sec by the application of mechanical force of 1.8 Hz frequency. The procedure to obtain porous PVDF film is schematically illustrated in Fig.6. Initially, ZnO nanowires were grown on a previously cleaned silicon substrate using hydrothermal reaction route, Fig.11a-c. The porous PVDF film was achieved by spin coating of PVDF gel on ZnO nanowires followed by etching of ZnO nanowires, Fig.11d-e. As depicted in Fig.11f, the dipoles of the as-obtained porous PVDF film were aligned using electric poling (20 kV/mm for 30 min at 80 °C). The digital micrograph and schematic representation of the as-designed multifunctional cell is depicted in Fig.11g and 12h, respectively. The as-developed meso-porous PVDF separator was considered beneficial to enhance the charge storing performance of the integrated cell. The improvement in the performance was credited to meso-porous structure of the separator that helped to facilitate the conduction of electrolyte ions through the separator. Moreover, it was identified that the meso-porous PVDF film could stock-up higher amount of electrolyte in comparison to quasi-bulk PVDF film. Likewise, Kim et al. designed a more efficient porous PVDF separator using ZnO nanoparticles that worked as pore site as well as nucleating agent to induce piezoelectric β -phase[48]. The output voltage of multifunctional cell using as-designed porous PVDF film was increased by 200 mV in 200 sec under the similar experimental conditions as used by Xing et al.[46].Therefore, developing porous piezoelectric separator in multifunctional cells is proven to be highly fascinating and could be vital in future development of multifunctional cells.

Figure.11. Schematic illustration of the fabrication process of PVDF meso-porous nano-structured film (a) previously cleaned silicon wafer the substrate, (b) deposition of seed layer on silicon substrate, (c) growth of ZnO nanowire on silicon substrate, (d) spin coating of PVDF gel on nanowires sample, (e) etching of ZnO nanowires in acidic medium, (f) illustration of the poling of PVDF film, (g) digital image of PVDF meso-porous film, and (h) Schematic illustration of the device design. Reproduced with permission from ref. [46], Copyright © 2014 Elsevier Ltd.

Recently, a multi-responsive cell that can be charged even by the application of human finger is developed. In addition, the electro-mechanical properties of the cell were found highly stable under continuous compression-release cycles[33]. The output voltage of the multi-responsive cell was found to be increasing from 500 mV to 832 mV in 500 sec under mechanical force of 1 Hz frequency[33]. The cell took 957 sec to discharge back to its original value under a constant discharge current of 1 μ A. The improved performance of the cell was credited to its highly flexible nature that was achieved using Kapton (poly (4, 4'-oxydiphenylene-pyromellitimide)) film as flexible support. As depicted in Fig.12a, the pressure exerted by the human finger was sufficient to drive electro-mechanical processes. By the application of finger pressing at a

frequency *ca.* 1 Hz ($F_1 < F_2 < F_3$), the multifunctional cell could be charged to 757 mV, 824 mV and 990 mV. Moreover, the multifunctional cell could be charged to 896 mV, 980 mV and 1010 mV, under compaction ($F_1 < F_2 < F_3$) caused by rolling bicycle tire at a *ca.* frequency of 1 Hz, as depicted in Fig.12b.

Figure.12. Charging of multifunctional cell by the application of (a) human finger, and (b) rolling compaction of bicycle tire, the discharging current is 1 μ A. Reproduced with permission from ref. [33], Copyright 2013, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

The performance of the multi-responsive cell was further improved by using symmetric electrode configuration and gel electrolyte instead of traditional asymmetric configuration (LiCoO_2 and graphite electrode) and Li based electrolyte[33,44,46]. Gel-electrolyte based multifunctional cells offered several advantages over Li based cells, for example, safer cell operation, high cell performance and ease of manufacturing. Recently, a symmetric multifunctional cell was designed using MnO_2 electrodes separated by a piezoelectric composite film of PVDF- ZnO [21]. The output voltage of the cell increased from 35 mV to 145 mV in 300 sec. The mechanism of charge storage was expected to be similar as explained earlier[44]. It is worth to mention that the transfer of electrons take place within the cell components, however, detailed mechanisms to provide clear insight is still not clear. Nevertheless, direct mechanical to electrochemical process has numerous advantages over other integrated devices; however, several improvements are still needed, such as development of flexible electrochemical cell, sealing of the electrochemical cell and straining of piezoelectric materials.

Figure 13. (a) Schematic illustration of multi-responsive cell, and (b) the output voltage as a function of time, Reproduced with permission ref. [49], Copyright © 2016 Elsevier Ltd

From the view point of multi-responsive cells, the charging rate can be slow due to the slow intercalation of ions into the electrode. As a result of the slow charging, the device is ineffective in storing energy produced from ambient mechanical perturbations applied for a smaller period. Moreover, the stability and the efficiency of the device are affected as it is subjected to mechanical impact for a longer period. Most recently, our groups developed a multi-responsive cell that has the ability to charge and discharge rapidly, as depicted in Fig.13. The charging time was improved by the use of CNT-based electrodes [49], in which charges are stored due to adsorption and desorption at the electrodes/electrolyte interface. The device showed an increment in the potential by 60 mV in less than 10 s of mechanical perturbation (70 N at a frequency of 5 Hz), thus facilitating fast charging self-powered/integrated supercapacitor.

The straining of piezoelectric separator in the electrochemical environment can be mitigated if piezoelectric material can be used as one of the electrode rather a separator. Xue et al. demonstrated the use of CuO/PVDF nano-composites in the cells without the need of piezoelectric separator[50]. By using this nanocomposite electrode, the output voltage of multifunctional cell could increase by ~100 mV in 240 sec under mechanical deformation of frequency of 1 Hz. The multifunctional cell took about ~90 sec to discharge with a loading current of 1 μ A. The improvement in the performance was assigned to the effective interconnect

between piezoelectric material and active electrode material, and a facile diffusion of electrolyte ions, as the device design does not involve a separator film.

4. Charging of supercapacitor by light

Solar energy is a sustainable energy solutions, however, batteries are required to take advantage of solar power[51]. Periodically replacement of batteries in off-grid solar panels is required. Using supercapacitors as an alternative energy storage unit, the cost and inconvenience of battery replacement can be mitigated up to some extent[52]. Supercapacitors are capable to store a relatively small amount of energy (in comparison to batteries), but they are most suitable when the energy demand of the system is intermittent. Solar powered lights are a perfect example of the coupling of solar, supercapacitor and LED technologies as an integrated solution. It must be noted that a supercapacitor device cannot be deep discharged unlike batteries, therefore, can be sustained for a long period of time. This coupling technology can be used in various applications, for example, street lights, garden lights, navigational aids, illuminated signs, traffic signals and park lights. However, the solar energy harvesting and energy storage technology are so far developed as the independent technologies. A multi-responsive integrated device will be highly valuable.

Recently, Wadhawan and co-workers developed a photo-galvanic cell (Indium-tin oxide glass as current collector) using photoactive molecule doped liquid crystals nano-system (e.g., lyotropic), and showed their promise as a supercapacitor cell[53]. The maximum light to electrical power conversion efficiency of *ca.* 2% could be achieved using this quasi-biphasic electrochemical system. The as-designed light-responsive cell was capable to generate an estimated energy density of 1 Wh/kg and power density of 1 kW/kg with a voltage efficiency of about 85%. In their demonstration, Brij 30 ((polyethylene glycol dodecyl ether, now known as Brij L4) was used as liquid crystal system, because of its attractive properties, such as self-assembly at room temperature in the form of bi-layer sheets separated by water layers. N-methylphenothiazine (PMe, of width 5 Å and length 12 Å) is chosen as the photo-redox active species, and $\text{Eu}^{2+}/\text{Eu}^{3+}$ redox couple was taken as the reducing agent. When the UV light was illuminated at one end of the ITO electrode, the oxidation of photo-chemically generated $\text{PMe}^{\bullet}$ took place on the same electrode (light electrode), while the reduction of Eu^{3+} occurred at the other electrode (dark electrode). Although, the change in open circuit potential or *emf* of the cell was fast enough (20

s), but the magnitude of the output voltage was little disappointing (~ 45 mV). Moreover, recovery of the cell electrochemistry in the dark conditions was pretty slow (typically 5 min.). The open circuit potential of the cell was improved to 1000 mV by altering the electrochemical reduction potential of metal ions; in other words, substituting Eu^{3+} with Zn^{2+} ions gives rise to higher cell voltage. To further improve the performance of the cell, Xia et al. designed a unique cell (three-electrode configuration), in which both oxidation (for energy storage) and reduction (for H_2 generation) reactions are captured effectively[54]. It is known that rational separation of photo-generated electron and hole can drive reduction and oxidation, respectively[54,55]. More precisely, photo-generated oxidative energy can be stored in supercapacitor via electrochemical reactions, concomitantly, the photo-generated reductive energy can be stored in H_2 through solar water splitting[54], an innovative concept as a multi-responsive supercapacitor.

The maximum solar to electrochemical conversion efficiency of *ca.* 0.2 % was achieved, which was about ten times lesser than photo-galvanic cell[53,56]. The lower conversion efficiency was credited to the poor photon-to-carrier conversion-efficiency of TiO_2 host[54]. The highest specific capacitance of 482 F/g was obtained at an applied current density of 0.5 A/g. In their multifunctional cell design, $\text{Ni}(\text{OH})_2/\text{TiO}_2/\text{FTO}$ was used as supercapacitor electrode for energy storage and Pt plat as H_2 production. Under solar irradiation, photo-generated holes oxidized $\text{Ni}(\text{OH})_2$, and raised 100 mV cell potential. To show the applicability of the design other electrode materials, such as NiO and $\text{Co}(\text{OH})_2$ were also used, however, the cell potential could not exceed 100 mV. Despite the fact that $\text{Ni}(\text{OH})_2$, NiO and $\text{Co}(\text{OH})_2$ are photochromic materials, nevertheless the color change does not contribute in the output voltage of multifunctional cell.

Zhang et al. proposed a new device design for multi-responsive cells using dye sensitized solar cell (DSSC) at the other end of the cell[57]. The as-designed cell offered photon-to-electricity conversion efficiency as high as 3.7%, which is much higher than previously reported multifunctional cells[54,56]. The cell potential could reach to ~ 90 mV under illumination, whereas, the electrochemical charge stored in the electrode materials was found to be about 2.1 C/g, corresponding to 1.4 mWh/kg energy density. In their cell design, as depicted in Fig.14a, the counter electrode was modified by PVDF (poly(vinylidene fluoride)) / ZnO nanowires composite for energy storage perspective. PVDF scaffold was common for both the catalytic

layer (Pt/Au) and charge storage ZnO nanowires. When the cell was irradiated under AM 1.5G for several minutes, photo generated electrons traveled from photo-electrode to counter electrode and divided onto two parts at the current collector, one via PVDF/ZnO nanowires to reach Pt layer and react with redox mediator for photo-electric conversion, and other was along ZnO nanowires and stored through the electric polarization of PVDF shell, the steps taking place during charge transfer as schematically illustrated in Fig.14b.

Figure.14. Schematics illustration of the (a) cell design and (b) mechanism of dye-sensitized solar cell with energy storage function, (c) open circuit voltage of multifunctional cell as a function of time, and (d) dependences of conversion efficiency and stored charge on the thickness of PVDF layer. Reproduced with permission from ref. [57], Copyright©2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

As shown in Fig.14b, some of the Li^+ ions were attached with the PVDF layer, which was due to polarization of PVDF shell. It is noteworthy that the thickness of PVDF layer plays an important role in achieving high conversion efficiency as well as charge density. As depicted in Fig.14c-d, PVDF layer thickness of 25 nm was found to be highly active to achieve both the highest cell potential and charge density besides its high conversion efficiency. It was hypothesized that an appropriate discontinuity in PVDF layer was helpful to improve the conversion efficiency, as in case of very thin (i.e., 16 nm) or very thick (i.e., 44 nm) PVDF layer due to large surface area of discontinuity or less discontinuity was not found favorable to improve the conversion efficiency.

The charge storage performance and conversion efficiency of the multifunctional cell can be further improved by improving the performance of counter electrode. In order to improve the performance, Yang et al. demonstrated the use of multiwall carbon nanotubes as a counter electrode for charge storage in DSSC[58]. The charge storage and conversion efficiency was achieved to be about 84% and 6.1%, respectively. Under illumination the cell potential could reach to 720 mV. The specific capacitance that could be obtained was 48 F/g. To further improve the charge storage performance of the multifunctional cell, a second phase material, i.e., polyaniline was incorporated with carbon nanotubes, and the specific capacitance as high as 208 F/g was achieved.

In their device design, unlike Zhang et al.[57], the electrolytes have been separated for efficient conversion and charge storage. When the MWCNTs were used as the counter electrode, the output voltage of the cell could reach to 720 mV in 44 sec. In contrary, when the counter electrode made of MWCNT-PANI was used, though, the cell voltage remained the 720 mV; while, the discharging time was found to be increased to 144 s. The longer discharging time indicates better charge storage ability of the composite film. At the counter electrode, part of the charges was further sent to photo-electrochemical cell and rest was stored by the energy storing unit (i.e., supercapacitor). In their observation, it was found that some of the charge was consumed in the supercapacitor cell that was ascribed to electrochemical reactions due to PANI. It was also identified that the thickness of counter electrode significantly affects the charge storage performance of the cell; it decreases with the increase in thickness. The cell voltage can be further improved by introducing the pseudocapacitive electrode materials in the charge storage unit. In this perspective, Yang et al. demonstrated the use of pseudocapacitive electrode

materials, i.e., hydrogenated ZnO core and ZnO doped amorphous-MnO₂ shell, in a stand-alone charge storing unit (integrated with DSSC), and could reach 2.4 V in 120 sec, however, the device was highly affected by the leakage current [59].

More recently, a novel multi-responsive cell is designed using polyaniline (PANI) as both photo-active as well as charge storage layer[60]. The photo-generated open circuit voltage could reach to 20 mV for shining the cell once with 1 sun, and it could reach to 50 mV after three successive illuminations. The uniqueness of the device was credited to the multi-responsive PANI layer. The specific capacitance of 140 F/g could be obtained at a current density of 2 mA/g. The preparation of the device and device design is schematically illustrated in Fig.15a. It must be taken into account that the device configuration takes PANI/CNT/PET and PANI/ITO/glass due to their different electronic conductivity order. The gradient in electronic conductivity is essential in redistribution of charge carriers generated during illumination.

Figure.15. (a) Schematics illustration the assembly process and structure of the device, (b-c) variation in the current density and voltage of the multifunctional cell during on/off of the light source. Reprinted with permission from ref.[60]. Copyright (2015) American Chemical Society

When the device was subjected to light illumination (AM 1.5 solar illumination of power density of 1 kW/m^2), the current density of the device reached 2 mA/g , in a short period of time. The observation of a small spike (Fig.15b) in the current profile can be ascribed to the negatively charged oxygen ions that were chemisorbed at the PANI surface. In their cell demonstration, the direction of current was from PANI/ITO/glass to PANI/CNT/PET electrode, as PANI/CNT/PET electrode works a photo-anode. As shown in Fig.15c, the device can be charged under illumination, and remain stable when there was no light. When the illumination was on, the photo-generated charges charge the energy storing unit (supercapacitor). When the illumination was off, the photo-generated charges were stop generating, but the supercapacitor was capable to

memorize the obtained voltage, and remained stable for long time. More recently, a solar energy harvesting flexible DSSC textile is reported that can store electrochemical charge of 0.36 mF/cm with a power conversion efficiency of 0.9% and prolong cycling stability. Under the illumination, the open circuit potential (OCP) of the cell can be reached 1.2 V in just 30 sec, and takes more than 70 sec to discharge in the dark at a current of 0.1 mA [61].

To harvest solar energy efficiently using the multi-responsive cell, intense attempts have been made to design photovoltaic and supercapacitor unit in the form of “layers or sandwich”. Poor conversion and energy storage efficiency have been observed in the planar configuration. The applications of planar configuration may be limited, as the cell cannot be retrofitted easily in flexible textiles. Chen et al. attempted to make a wire shaped multifunctional supercapacitor device alternatively “energy-wire”[62]. The energy wire was capable to produce a conversion efficiency of 1.5 % with a length capacitance (or areal capacitance) of 0.024 mF/cm (or 0.6 mF/cm²). The energy conversion efficiency of the device was about 68.4%, where the output voltage of the device could reach to 600 mV. The output voltage and the storage-efficiency of the energy-wire were highly competitive to planar structured multifunctional cells[57–60]. An energy density of 0.15 $\mu\text{Wh}/\text{cm}^2$ can be achieved using energy-wire. In their cell design, a titanium wire was modified in segments with aligned TiO₂ nanotubes on the surface. The diameter of the nanotubes was about 50-100 nm, and wall thickness varied between 15-50 nm. N719 was used as photo-harvesting material and decorated on modified Ti wire. CNT fiber and Ti wire worked as electrode for energy-storage and photo-conversion, respectively. Under illumination, the photo-generated electrons transported from Ti wire to CNT fiber, where part of the electrons are sent to photo-sensitive region and rest are stored in CNT electrode. The energy-wire was discharged at a current of 0.1 μA , when the connections were disconnected. The energy-wire produced an output voltage of about 600 mV, which is higher than the planar structure.

CNT fibers were found to play a vital role on the effective realization of energy-wire. It was also observed that the photo-conversion efficiency of the energy-wire could be further improved by increasing the length of TiO₂ nanotubes. The unique wire structure enables novel and promising applications, for instance, it is envisioned that it can be effortlessly incorporated into electronic

fabrics by a well-defined weaving technique that serves as a self-powering unit for portable electronic gadgets and equipments.

5. Charging of supercapacitor by heat

Harvesting or utilizing thermal energy, particularly in the low temperature range ($<250\text{ }^{\circ}\text{C}$) has attracted significant attention in the recent years[63–66]. In the low temperature range, direct utilization of the thermal energy is challenging due to several reasons, for instance low energy density in the low grade heat[67,68], therefore, harvesting this low grade heat is of great importance. Classically known thermal to electricity conversion technique, which is based on Seebeck effect, is apt to high grade heat, however, it does not work efficiently in the low temperature range[69]. It must be noted that Seebeck effect is not the only factor governing the direct utilization of waste heat to electric energy, temperature induced capacitive effect is distinctly one of the other factors.

Figure.16. Schematics illustration of the thermally-charged supercapacitor or multifunctional cell, © IOP Publishing, Reproduced with permission [70], All rights reserved

Lim and co-workers[70] found that the potential of two electrodes (symmetric cell) constructed with high surface area nano-porous carbon can be altered by the external heat (illustrated in Figure 16); in other words a potential difference can be created by altering their temperature. When the two electrodes were connected, charges start moving from high temperature electrode to low temperature electrode to establish a new thermal equilibrium, and converting the absorbed

heat to electric energy. The capacitive phenomenon has numerous advantages over the well established Seebeck effect, for instance, mitigating the thermal shorting, as the motion of the charges and thermal conduction can be separated.

To validate the phenomenon of thermal capacitance, a nano-porous electrode system of surface area 500 m²/g and pore distribution 1-10 nm was used to design a supercapacitor device, where sodium chloride (26 wt%, NaCl) was taken as electrolyte[71]. The temperature of one electrode was raised with a rate of 2 °C/min, while the other electrode remained at ambient conditions. With the small change in temperature, an output voltage of more than 100 mV was obtained. The coefficient of thermoelectricity or Seebeck coefficient was found to be 3.7 mV/C, which was two-order of magnitude higher than the conventional thermoelectric material[72]. It is worth mentioning that the time required to set up a new equilibrium is proportional to the electrochemically active surface area of the electrode.

Commonly, it is known that as the amount of capacitive charge stored is proportional to the concentration of the electrolyte ions[73]. However, thermally capacitive charge does not vary linearly with the increase in the electrolyte ions, as investigated by Lim and co-workers[25]. To address this peculiar behavior, the authors assumed that the origin of thermally capacitive effect lies in the nano-porous structure of the electrode, and the inner ion concentration in the nano-pores does not vary much with the change in ion concentration, thus the output voltage. However, recent studies showed that the ions population in a nano-porous electrode varies linearly with the ion concentration in bulk[74]. It remained unclear, how do the Faradaic reactions affect the thermal voltage or charging process of supercapacitor until the recent work by Wang et al.[75]. In their investigating it was found that at relatively higher temperature (65 °C) the underlying mechanism is thermo-electrochemical processes that enhance the kinetics of Faradaic reactions at the interface. It is identified that the electronic charging (activation step) is crucial in order to initiate the thermal charging.

The mechanism of thermo-electrochemical process is illustrated schematically in Fig.17[75]. Fig.17a shows potential of two electrodes in equilibrium and their respective electronic energy diagrams. $\mu_{surface}^{-pos}$ and $\mu_{surface}^{-neg}$ denote the electrochemical potential required to initiate the Faradaic reaction at the positive and negative electrode, respectively. Any changes in the electronic energy of positive ($E_{F,pos}$) and negative ($E_{F,neg}$) electrode instantly develop a potential,

i.e., voltage of electrochemical double layer capacitor. As shown in Fig.17b, the moment when supercapacitor is charged, $E_{F,pos}$ becomes more positive and $E_{F,neg}$ becomes more negative, as the electrons are removed and added into the electrode, respectively. In the meantime, functional groups attached with positive electrode start oxidizing due to removal of electrons, whereas, reverse behavior occurred at the negative electrode. Due to sluggish Faradaic reactions of the functional groups on positive electrode, the electrochemical redox potential was found less positive with respect to fast electrode reactions, whereas, it was less negative on the negative electrode side. After discharging (Fig. 17c), the energy of the electrodes regains their original positions, however, the functional groups could not retain their original electrochemical redox potential in the given span of time (1800 sec). The kinetics of regaining the original positions of electrochemical redox potential could be expedited at elevated temperature. During thermal charging of the device, $E_{F,pos}$ becomes more positive due to loss of electrons that were consumed by the oxidized functional groups attached at the electrode surface, converse is true for $E_{F,neg}$, as depicted in Fig.17d. The difference between electrochemical redox potentials, i.e., $\mu_{surface}^{-pos}$ and $\mu_{surface}^{-neg}$ gave rise to output voltage, as presented in Fig.17e.

Figure.17. Schematics illustration of the mechanism of thermal-charging, (a) the initial voltage of the cell after shorting is 0 mV, which corresponds to state **a** in (e), (b) cell is electrically charged to a high voltage V_0 , which corresponds to the process 1 in (e), (c) cell is then electrically discharged and shorted at 0 mV again, which corresponds to process 2 in (e), (d)

Process of the “thermal charging” of the cell in hot water $\sim 65^{\circ}\text{C}$, which corresponds to the process 3 in (e), (e) stepwise illustration of the mechanism of the thermal-charging of multifunctional cell. Reprinted with permission from Ref. [75]. Copyright (2015) American Chemical Society

The output voltage of thermo-electrochemical processes strongly depends on the history of the thermal charging\discharging. It is identified that after each thermal charging the successive thermal charging was unable to reach maximum output voltage. The plausible mechanism of this behavior could be explained as follows. After the first thermal charging, $E_{\text{F,pos}}$ and $\mu_{\text{surface}}^{-\text{pos}}$ were aligned with each other. In the successive discharging process, both $E_{\text{F,pos}}$ and $\mu_{\text{surface}}^{-\text{pos}}$ start moving upward, where, $E_{\text{F,pos}}$ acquired the original position quickly, while, $\mu_{\text{surface}}^{-\text{pos}}$ could not aligned with $E_{\text{F,pos}}$ due to sluggish Faradaic processes. In the following thermal charging, the output voltage corresponded to an electrochemical potential that was required to establish a new equilibrium, however, it was found to be gradually decreasing due to less amount of potential required to establish a new equilibrium.

Figure.18. Voltage profiles of the multifunctional cell during activation steps with different electrical charging voltage cutoff, (b) the output voltage profiles of the multifunctional cell corresponding to each activation step (c) Voltage profiles of the multifunctional cell at different applied current densities, (d) the output voltage profiles of the multifunctional cell corresponding to each applied current densities,(e) effect of the activation step on the output voltage of the

cell,(f) the output voltage profiles of the multifunctional cell corresponding to each activation step. Reprinted with permission from Ref. [75]. Copyright (2015) American Chemical Society

The electronic charging/discharging (activation cycles, current density, maximum voltage) history of supercapacitor also plays a crucial role in deciding the output voltage of thermo-electrochemical process. One of the observations was that the thermally charged voltage was higher for the supercapacitor charged to higher voltage, as can be seen in Fig.18a-b. At higher electronic potential, more functional groups were prone to be oxidized /reduced that leads to develop a higher difference between electronic and electrochemical potential, and thus the voltage output. The other observation was that the rate at which supercapacitor was charged significantly affects the output of multifunctional cell, as shown in Fig.18c-d. The mechanism could be elucidated by the fact that less surface functional groups were oxidized /reduced during fast electronic charging, as the diffusion limited charge transfer kinetics of Faradaic processes could not cope with the electronic effects. The strength of oxidation/reduction of surface functional groups was accountable to develop electrochemical potential[76]. Moreover, the effect of the activations steps was also observed on the thermally charged voltage of supercapacitor, as presented in Fig.18e-f. More surface functional groups could be oxidized/reduced when it was twice activated, therefore, more potential was required to achieve the equilibrium state, and hence the higher output voltage.

6. Other unconventional means to charge supercapacitor

As discussed in the previous sections that the electrochemical reactions can be activated by altering their local chemical environment. It is known that the energy produced during electrochemical processes in enzymatic cell is high enough to drive small portable electronic devices[77,78]. In the biological processes the energy is originated from the reduction of oxygen at cathode and oxidation of an organic fuel on the anode[79]. Recently, a multi-responsive cell based on bio-electrochemical processes is reported[22]. The as-designed bio-device was the combination of supercapacitor and enzymatic fuel cell. The bio-anode and bio-cathode was prepared by modifying the surface of Au nano-particles using *Corynebacterium thermophilus* cellobiose dehydrogenase (CtCDH) and *Myrothecium verrucaria* bilirubin oxidase (MvBOx), respectively, while capacitive surfaces are prepared by modifying the conventional graphite paper using CNT/polyaniline. The output voltage of the cell was found to be increased from 100

mV to 400 mV in 7200 sec. In the literatures, it was emphasized that the bio-supercapacitor was not optimized correctly, neither on the charging nor capacitive side[22]. The performance of the cell can be further improved by adapting the following strategies, a) determining the appropriate ratio between the capacitive and charging components, b) a proper selection of highly stable but efficient bio-elements, c) ensuring the covalent attachments of bio-elements and nano-composites to the electrode surface, d) mitigating the leakage currents, and so on.

It is accepted that in the electrochemical energy storage devices, insertion and extraction of the ions takes place within the electrode or in the close proximity, which leads to chemical changes in the material[80,81]. The chemical changes can be reflected by changing their color accordingly, this change becomes apparent when they are designed on a transparent current collector[82]. The phenomenon of change in optical modulation by the application of applied voltage is known as electrochromism. A reversible surface-redox reaction takes place at the interface of the electrode/electrolyte in electrochromics. The fast surface adsorption/intercalation of electrolyte ions in the electrode material (e.g., V_2O_5 , NiO, Persian blue, etc.)[83–85], enables the visualization of energy density by apparent change in color. Electrochemical energy storage devices and electrochromic windows have many aspects in common, for instance, electrode materials, cell configuration, mechanism of physical and chemical operations. The colored and bleach state of an electrochromic window is comparable to charge and discharge state of an electrochemical energy storage device, respectively[86]. In other words, an electrochromic window is a rechargeable electrochemical energy storage device with transparent electrodes. Wang et al. demonstrated the use of Prussian blue in electrochromic as well as electrochemical energy storage device simultaneous[87]. Several other research groups have demonstrated the concept (organic as well as inorganic) in which charge and discharge state of the device can be visualized [83,88,89]. Most recently, Cai et al. introduced an integrated electrochromo-supercapacitor device, in which the state of the charge could be clearly visualized by the change in color of the device[89], as depicted in Fig.19.

Figure 19. Schematic illustration of the state of the charge and color of the electrochromo-supercapacitor device, reprinted (adapted) with permission from ref.[89], Copyright (2016) American Chemical Society.

The transmission during colored and bleached state of the electrochromo-supercapacitor was found to be 30% and 95%, respectively[85]. It is obvious that during charging electrolyte ions adsorbed or intercalated into the materials structure, the optical transmittance in the charged state was found to be about 30%. The highest specific capacitance that could be obtained in electrochromo-supercapacitor was 221 F/g at an applied current density of 1 A/g. From view point of indoor and outdoor practical applications, electrochromic behavior of large scale (15 cm x 15 cm) charge storing glass window has also been demonstrated [90]. More recently, Yang et al. comprehensively summarized different means to store electrochromic energy in various materials system, including inorganic, organic and hybrid systems [91]. The concept of designing electrochromo-supercapacitor is relatively new and significant research is in progress to further improve the performance of these integrated devices.

7. Summary and outlook

In summary, multi-responsive electrochemical energy storage devices are presented that can be charged and responded to various forms of stimuli such as energy, for instance, temperature, light, mechanical pressure, and biological processes. The multi-responsive cells are designed in such a manner so that the energy can be simultaneously harvested and stored without affecting

the working cycles of the other components. In the mechanical responsive electrochemical cells, a piezoelectric separator film is used that work as both a separator and a piezoelectric potential generator. The intensity of the piezoelectric potential can be altered by optimizing piezoelectric materials. The mechanism of the energy storage or the movement of electrons within the cell warrants more understanding to realize its potential.

The mechanical energy that involves sliding, bending rather than compression can also be harvested using the platform of multi-responsive electrochemical energy storage devices. The voltage produced contains fraction of alternating current that can be filtered by using a full-wave bridge rectifier, and the filtered voltage can be used to power-up an electrochemical cell. Nevertheless, only a fraction of generated voltage can be stored. Due to the versatile flexibility and ease of fabrication, the self-charging cells can perhaps be incorporated into complex and designer textiles, more efforts are required to design other flexible components, such as rectifier and impedance balancing circuit into the wearable multi-responsive electronic textiles.

The conversion of solar energy into electrical energy can be performed using multifunctional electrochemical energy storage devices. Numerous advantages, including stable cell operation, excellent charge storage efficiency and ease of fabrication can be experienced using these multifunctional devices. However, a lot of parameters still have to be improved in order to maximize the performance of the cell. One of the most vital parameter is conversion efficiency, which is barely 2% in the best cases has to be improved significantly. One of the reasons of such poor conversion efficiency could be the integration of the suitable energy storage electrode material and highly transparent current collector. Moreover, the adsorption of electrolyte ions on the surface of the energy storage electrode material (typically a counter electrode in these configurations) could be a critical factor to affect the performance of the multifunctional electrochemical energy storage device.

Harvesting low-temperature waste heat using supercapacitor is one the fascinating area of research as the traditional heat energy harvesting devices (based on Seebeck effect) do not work effectively below 250 °C. Multi-responsive electrochemical energy storage devices could harvest the heat energy at a nominal temperature of 60 °C. So far the reported devices are based on carbon based materials, in which the harvested waste energy is utilized to power-up a cell. To facilitate the heat assisted charging of the device, electrical activation of the device is

recommended. We anticipate that emerging advanced integrated technologies and new electrode materials will bring excellent performance that allow multi-responsive electrochemical energy storage devices to enable convergence of energy conversion technologies.

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