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Review Article

Recent enterprises in high-rate monolithic photoelectrochemical energy harvest and storage devices Daniel Turner, Ming Li, David Grant and Oluwafunmilola Ola

Abstract

Solar energy is set to play a major role in decarbonising the economy and creating a zero-emissions future. However, there is a need to store this abundant energy and, in many instances, supply that energy at a high rate. With large expense and efficiency losses in integration through external circuits, a monolithic two-electrode harvest storage device or photosupercapacitor with a high-power density and stable life cycles is an exciting challenge. Here we review the most recent advancements in photo-supercapacitors and some approaches to overcoming various challenges to delivering a marketable device.

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Introduction

Recently the investigations into renewable energy sources have increased due to the well-known problems associated with the reliance on finite fossil fuels. One of the forerunning renewable energy sources is solar, which is not surprising with \sim 739kWm⁻² incident on the Earth at the surface from the Sun $[1,2]$ $[1,2]$ $[1,2]$. With the power conversion efficiency (PCE) of solar cells rising year on to the point of over 20% for many cell types, the technology has improved greatly [[3\]](#page-6-2). However, due to the intermittence of the Sun storage solutions are necessary. While being possible to couple harvest and storage devices via external circuitry, this is expensive and inefficient. Thus, the investigation into integrated photo-electrochemical energy storage

technology has been extensive in the latter days $[4-11]$ $[4-11]$ $[4-11]$ $[4-11]$. Electrochemical energy storage devices (EESD) work via Faradaic processes, in secondary batteries these processes are slow, and diffusion controlled (minutes to hours), while in supercapacitors (SC) the processes are surface bound and fast (well under a second to a minute) or based on the non-Faradaic electric double layer (EDL) at the electrode electrolyte interface. It is possible to become confused about where the battery/SC line is drawn and sometimes an electrode material or device is reported as an SC while displaying more battery like behaviour being more suitable to the category of high-rate electrochemical (HREC) or supercapattery electrode [\[12](#page-7-1),[13](#page-7-2)]. Despite the publication of excellent discourses on the correct way to report [[12](#page-7-1),[14](#page-7-3)[,15](#page-7-4)], there are reports of so-called "pseudocapacitive" materials detailing high specific capacitance and related energy and power while they display nonlinear Nernstian or battery like qualities $[16-19]$ $[16-19]$ $[16-19]$ $[16-19]$. Notwithstanding, it must be pointed out, possibly inflated energy capacity of these devices/materials, the fact remains that the charge capacity increases with illumination thus making them viable candidates as photoelectrode material for high-rate photo-electrochemical storage devices. For a material with a capacitive rectangular CV curve eq. [\(1\)](#page-0-0) can be used to find specific capacitance (C_s) in F/g; for a non-capacitive CV, specific charge (Q_s) in C/g can be found from eq. [\(2\)](#page-0-1). \overline{v}

$$
C_s = \frac{\int_{V_1}^{V_2} I(V) dV}{m \cdot \Delta V \cdot v}
$$
 eq.1

$$
Q_s = \frac{\int_{V1}^{V2} I(V)dV}{2 \cdot m \cdot v}
$$
 eq.2

Where $\int I(V)dV$ is the area enclosed by the CV curve, m is the active mass of the electrode material, ΔV is the potential window and ν is the sweep rate $[5,12,14,15,20-22]$ $[5,12,14,15,20-22]$ $[5,12,14,15,20-22]$ $[5,12,14,15,20-22]$ $[5,12,14,15,20-22]$ $[5,12,14,15,20-22]$ $[5,12,14,15,20-22]$ $[5,12,14,15,20-22]$ $[5,12,14,15,20-22]$ $[5,12,14,15,20-22]$. Using the discharge of the GCD of a material can give C_s (eq. (3) or Q_s (eq. (4)).

$$
C_s = \frac{I \cdot \Delta t}{m \cdot \Delta V} \qquad \text{eq.3}
$$

$$
Q_s = I \cdot \frac{\Delta t}{m} \qquad \qquad \text{eq.4}
$$

Where *m* is the mass or area of active material (e) : *I* is the current; Δt is the time of discharge (s); and ΔV the potential window (V). A good example of Faradaic capacitance was reported by Chen et al. using $Ni(HO)_2$ storage material coupled with $TiO₂$ that displayed a near linear GCD and C_s of 22.9 mF/cm², showing good "Pseudocapacitance" [\[12](#page-7-1),[23\]](#page-7-8).

The EESDs that include SCs and HRECs or "supercapatteries" are possibly the most important energy storage devices with advantages of high-power density from fast charge/discharge rates, long and stable cycle life from the absence of phase change of electrode material, and often at relatively low cost, potentially using "green" chemistry [[12](#page-7-1),[24](#page-7-9)]. Herein we concentrate on the most recent developments in the field of so-called photo-supercapacitors (PSC) that lend themselves to applications such as mobile devices, devices on the IOT, wearable devices for fitness and medical sensors or integrated into zero emission buildings (ZEB) [\[25](#page-7-10)–[32\]](#page-7-10).

Architecture, mechanisms, and applications

There are several different architectures for fully monolithic integrated devices. One of the main characteristic distinctions is the number of current carrying electrodes (CCE), generally two or three [\[4](#page-7-0)]. There will be CCEs attached to a photoelectrode or photovoltaic (PV) and counter electrode in a two-electrode device with various charge storage mechanisms involving the electrodes and electrolyte, [Fig. 1](#page-2-0) a. While in a threeelectrode device, there will be a bridging CCE (BCCE) between the counter electrode of the harvesting device and one of the storage element electrodes in either a uniaxial [Fig. 1](#page-2-0) C or biaxial configuration, [Fig. 1](#page-2-0) b.

While a two-electrode device has benefits due to the cost and weight of the electrode material being the greatest expense, a three-electrode device is easier to configure as existing technology can be used with a suitable low-resistance BCCE. For the photo-energy capture element, PV, dye-sensitised solar cell (DSSC) and organic semiconductor solar cell (OSSC) can be used; for the storage element the easy-to-configure and fabricate, symmetric electric double layered capacitors (EDLC) return favourable and low-cost results $[33-36]$ $[33-36]$ $[33-36]$. However, the use of a symmetric Pseudocapacitor reportedly returns higher capacitance ([Table .1](#page-3-0)). Das et al. in one instance used a polymer PAAQ as both CE and SC electrodes. To increase charge transport in CE they incorporated CoTe nano-rods while the SC electrodes were naked and suffered from swelling via redox reactions. Subsequently, they used a different polymer PProDOT decorated with Bi nanoflakes and carbon microspheres to prevent swelling and increase charge transport [\[37,](#page-8-1)[38](#page-8-2)]. To increase the stability and reduce the mass of the device all devices reported of late

used gel electrolyte, this also negates the need for separate packaging and removes the issues of liquid electrolyte leakage. The BCCEs used, range from ITO coated glass, FTO coated glass, carbon fabric, and nickel-foam for devices in a biaxial configuration while Berestok et al. used a conductive epoxy for devices in a uniaxial configuration $[33-38]$ $[33-38]$ $[33-38]$ $[33-38]$ $[33-38]$. Using PET electrode/ substrate material coupled with flexible OSCs can reduce mass and volume while creating a flexible device with a thickness of as little as 43 microns. Liu et al. and Qin et al. used different SC storage parts, polymer CNT mix and MXene respectively. Qin reported massive volumetric capacitance ([Table .1\)](#page-3-0) due to the thinness of material; both devices showed great promise as the basis of self-powering flexible wearables [\[39](#page-8-3)[,40](#page-8-4)].

The greatest challenge with a two-electrode configuration is finding a multifunctional electrode material that efficiently harvests, separates, and stores charge. In the search for a photo-sensitive capacitance electrode material, several use a transition metal oxide (TMO) as they show good stability, are relatively cheap, abundant and pose few environmental issues in comparison with e.g., lead containing hybrid perovskite $[41-44]$ $[41-44]$ $[41-44]$ $[41-44]$. The investigation of hybrid materials and the junctions within promises to offer an answer to the challenge. Momeni et al. investigated the effectiveness of a different TMO deposited to assist the already wellperforming $WTiO₂$ nanotube arrays as a photo-assisted supercapacitor. The metal oxides they chose were the well reported alternatives to the problematic but high performing RuO_2 ; V_2O_5 and MnO_2 [\[45,](#page-8-6)[46\]](#page-8-7). The addition of TMO not only shifts the bandgap into the visible spectrum but also reportedly increased surface area and behaved as excellent charge storage sites [[44](#page-8-8)]. The materials' synthesis route affects the morphology and thus its' efficiency as shown by Chatterjee et al. and Altaf et al. The latter found lower crystal dimension and fewer defects causing a greater increase in Coulombic efficiency under illumination while the former found a smaller particle size aided in transport of ions for storage $[42, 47]$ $[42, 47]$ $[42, 47]$ $[42, 47]$ Further to the use of transition metals within electrodes is the use of metal ion, i.e. Zn or Mg, in PSC electrolyte explored by Boruah et al. with either photocathode or photoanode storing appropriate ions on charging $[48-50]$ $[48-50]$ $[48-50]$ $[48-50]$. Isaqu et al. demonstrated the successful use of $Bi₂S₃$ as sensitizer in DSSC, CE and storage element in a device finding the addition of MWCNT gave better electrocatalytic behaviour and reversibility, with reduced electrode/ electrolyte resistance, higher conductivity and faster ion diffusion leading to superior catalytic activity [[51](#page-8-12)]. Investigating the charge storage mechanism of organometallic-halide perovskite PSC (methylammonium bismuth iodide) Popoola et al. using an altered Dunn's equation (eq. 5), to include lightinduced current in CV scan $(eq. 6)$, found the lightinduced current fell from 99 to 78% at a rate of

 $I_{mD}(V) = I_D(V) + \chi(v)$ eq.6

found, by plotting, as the intercept and gradient for that

Where $I_{mD}(V)$ is the light modified current and $\chi(v)$ is the light induced current. While this is illuminating, going forward it may be interesting to probe the diffusion and surface ratio of current around the max light induced

potential at that scan rate.

 $0.01-0.50$ V/s respectively showing very strong lightinduced energy storage mechanism [[12](#page-7-1),[15](#page-7-4)[,47,](#page-8-10)[52\]](#page-8-13).

$$
I_D(V) / v^{\frac{1}{2}} = c_1 \left(v^{\frac{1}{2}}\right) + c_2 \quad \text{eq.5}
$$

Where $I_D(V)$ is the current at a specific potential, $v^{\frac{1}{2}}$ is the square root of the scan rate while, c_1 (the surface-bound current) and c_2 (diffusion controlled current) can be

Figure 1

Various PSC device architectures (a) two-electrode planar uniaxial strategy based on a heterojunction PV and symmetric SC showing charge transfer route. Reproduced with permission from Ref. [\[43\]](#page-8-14) Creative Commons. (b) A three-electrode biaxial parallel planar strategy based on DSSC and sym-metric SC. Reproduced with permission from Ref. [[38\]](#page-8-2) Copyright Elsevier. The charge discharge path of a uniaxial 3 electrode device with p-n junction incorporating symmetric supercapacitor. Reproduced with permission from Ref. [[34\]](#page-8-15) Creative Commons (d) photo-chargeable electrochromic energy-storage device utilising nanostructured WO₂ as charge storage and light shading element in a smart window. Reproduced with permission from Ref. [\[31](#page-8-16)] Copyright Elsevier. (e) Fibre type device with the counter electrode of the DSSC harvest element utilised as one of the storage element electrodes. Reproduced with permission from Ref. [\[26](#page-7-11)] Creative Commons.

Abbreviations: PAAQ – poly (1-aminoanthraquinone), PMMA – Poly(methyl methacrylate), BPE – blend polymer electrolyte, PVP – Polyvinyl pyrrolidone, PVA – Poly(vinyl alcohol).

HOIP – halide organic inorganic perovskite, MPNC – mesoporous nano-carbons, P3HT – poly (3-hexylthiophene-2,5-diyl), PC60BM – phenyl C60-butyric acid methyl, MWCNT – many walled carbon nanotubes, SNGP – Sulphur and nitrogen doped graphene particles, PProDOT – poly(3,4-propylenedioxythiophene), CMS – carbon micro-spheres, BiNF – bismuth nano-flakes.

PBDTTT-OFT – poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b; 4,5-b']dithiophene-2,6-diyl-alt-(4-octyl-3-fluorothieno[3,4-b]thiophene)-2-carboxylate-2-6-diyl], PC₇₁BM – [6,6]-phenyl-C₇₁-butyric acid methyl ester, PEDOT - Poly(3,4-ethylenedioxythiophene), PSS - polystyrene sulfonate, PM6 - Poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)], Y6 – Non fullerene acceptor Y6 (C₈₂H₈₆F₄N₈O₂S₅).

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Table 1

current scan rate at various power densities of illumination. It is also important to note this doesn't discern between the Faradaic and non-Faradaic processes at the surface.

To further improve device efficiency, internal resistance on discharge due to junction or Schottky barriers needs to be addressed [\[53,](#page-8-25)[54](#page-8-26)]. Interrogation of charge separation, transport and storage mechanisms are important to better understand devices and achieve higher efficiencies. Wenjun et al. investigated and reported on the concept of a Faradaic junction, a mechanism by which there is an exchange of electrons and ions at a Faradaic material (farador) electrolyte interface during a photoexcitation within a semiconductor interfaced with a farador. The charge carriers are therefore a mix of both with the ionic charge being stored in the farador at or on the surface. By blocking the short circuit between the farador and the CCE by the judicious use of a semiconductor, capacitance is increased with a negligible potential barrier between the farador and short-circuited CCE but the potential window of the farador is affected by the Fermi level of the semiconductor. This barrier height can be controlled by the band position of the semiconductor [\(Fig. 2](#page-4-0) a) [\[54\]](#page-8-26). Two junctions in a planar sandwich configuration were fabricated, one with $WO₃$ and the other with $MoO_{2.5}$, photo-electrodeposited on n^+p-Si substrate. Comparing the photo charge and dark discharge activity of the junctions with that of the same deposited on carbon substrates, it was shown, the potential window can be shifted by a semiconductor while maintaining the dis/charge behaviour. The first 2 electrode photo-supercapacitor that can discharge without an applied bias via the adjusting potential was devised, evidenced by experimental CV plots [\[55](#page-8-27)]. They used the theory of faradaic junction to explain greater than theoretical open circuit potential (OCP) of semiconductor/semiconductor interfaces such as quantum dot sensitised solar cells or perovskite solar cells and high photovoltages. In situ techniques were used to support the theory that the junction promotes photo-driven surface Faradaic reactions within $TiO₂/CdS$ on the T_1O_2 surface only, due to the potential window favouring the Faradaic charge/discharge process on TiO₂. This reaction seemingly occurred only on the surface not in the bulk and was promoted by the swift charge transfer between the $TiO₂$ and the CdS [[56\]](#page-8-28). Subsequently, a twoelectrode photo-rechargeable Faradaic junction device was created, which exhibited a photovoltage memory effect; the discharge voltage matching that of the photovoltage which in turn promotes high performance. This effect didn't occur with all CEs while probing the effect via a real-time OCP measurement method; the OCP (between SCE and working electrode) for the photoelectrode (PE) and the CE in a disconnected dark stage, a connected dark stage, a connected light stage and back to a disconnected dark stage. It was apparent

a. Band diagrams of the interfaces between current carrying electrode (CCE)/Faradaic layer (farador)/electrolyte; and CCE/semiconductor/farador/ electrolyte under an applied potential. ΔV is the barrier height created by eliminating the short circuit between farador and CCE, with the choice of semiconductor (band gap) and farador (redox potential) tuning the barrier [\[54\]](#page-8-26). b. Schematic of working prerequisite for the photovoltage memory effect in a solar rechargeable device. V_1 and V_2 are a lower and upper limit of Faradaic potential window of a Faradaic material in a photoelectrode, respectively; V_1 ' and V_2 ' are a lower and upper limit of Faradaic potential window of a counter electrode, respectively; V_F is an equilibrium potential of a counter electrode. V_{oc} is a photovoltage in a photoelectrode. To realize a photo-oxidization of a Faradaic material on a semiconductor, the hole quasi-Fermi level (E_{Fp}) in a semiconductor should be more positive than V₁ and more negative than V₂, that is, V₁<V_E + V_{oc}<V₂. On the other hand, if photo-generated electrons from a semiconductor can reduce the Faradaic layer, not the electric double layer of a counter electrode, V_E should be more positive than $V₁$ ' and more negative than V_2 ' (V_1 '< V_E < V_2 ') Wang et al. 2022 [[57](#page-8-29)].

Table 2

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Abbreviations: HEMIm/BF₄ – 1-(2-hydroxyethyl)-3-methyl imidazolium tetrafluoroborate, rGO – reduced graphene oxide, TCE – transparent conductive electrode, PTB7-Th – Poly[4,8-bis(5-(2-ethylhexyl) thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2-6-diyl)], CNTY – carbon nanotube yarn.

"side reactions" occurring under zero bias were trivial and lead to 100% Coulombic efficiency over 80 cycles also proving excellent reversibility. Due to the photovoltage memory effect, a higher performance occurred from "increased storage time and higher charge quantity of the faradaic layer than the electric double layer". With the careful choice of semiconductor, farador and CE the onset potential, photovoltage and discharge voltage can be controlled [\(Fig. 2](#page-4-0) b). The discovery of the mechanism of tuning semiconductor band gap and Fermi level to farador equilibrium potential and Faradaic potential window along with the CE equilibrium potential and Faradaic potential window is key to designing high energy-dense two-electrode devices [\[57\]](#page-8-29).

An important application of PSCs will be in zero emission buildings (ZEB). There have been several recent investigations into this application. Orozco-Messana et al. investigated a heterojunction PV coupled with a SC incorporated within a porous stoneware tile as near ZEB material [[29\]](#page-7-13). They decided on a TMO heterojunction PV as the "best compromise" between efficiency, simplicity and durability. The storage element was a modified rGO with pseudocapacitive $Ni(OH)_2$ coupled with an electroless deposited conductive layer of $Ni-Mo-P$ as an adherence agent to the porous porcelain substrate. The conductive layer showed good adhesion for the metal layer and low resistivity of 7.2 MPa and 10.6 $\mu\Omega$ cm respectively. They recorded good capacitive stability over 200 cycles [[30](#page-7-14)]. Photo-electrochromic capacitors (PESC) as smart windows to regulate a building's temperature and light ingress with solar energy capture/storage have been investigated $[25,28,29,31]$ $[25,28,29,31]$ $[25,28,29,31]$ $[25,28,29,31]$. TiO₂ based DSSC were commonly used to charge with the redox action of electrochromic $WO₃$ to store energy as intercalated ions balancing the negative excitons from the DSSC causing the darkening [\(Fig. 1](#page-2-0) d. [\[31\]](#page-8-16)). Yin et al. successfully overcame the limiting diffusion speed and electrolyte driven corrosion of the electrode by incorporating $WS₂$, the further inclusion in the DSSC CE also increased conductivity. Not only did the stored energy drive the electrochromic action but could be used on discharge for external load [[25](#page-7-10)]. Liu et al. also produced a PESC complimented with Prussian blue dye. The combination of electrochromic chemicals gave a multimodal material working in original, bright, cool and dark modes. As a future development of this excellent technology the driving potential to trigger the Dark mode, for total blockage of light and heat, could be better supplied from the stored photo-charge $[28]$ $[28]$ $[28]$. Zhang et al. reported on a flexible PESC; the conductive contact substrate was ITO-PET which shows low sheet resistance and high transmittance. Its flexibility allows for smart windows of all shapes and wearable applications [\[29\]](#page-7-13). An alternative route to wearables is fibres; Jin et al. used an existing printing technique to embed metal strips into a UVcurable conducting polymer creating a stable, flexible

OSC SC strip device that was then woven into a textile [\[32\]](#page-8-38). Another investigation into a fibre style PSC came from Kim et al. using a novel method of "floating catalyst" CVD [[58\]](#page-9-2) to create threads of CNT that were subsequently spun into yarn and then appropriately doped. The device showed great stability even after 10 cycles of automatic washing [\(Table 2\)](#page-5-0) [[26](#page-7-11)]. These kinds of application innovations certainly bring us one step closer to marketable devices, a comparison of storage capacity and stability of recent two-electrode devices can be seen in [Table 2.](#page-5-0)

Conclusion

In reviewing the most recent advancements in the area of PSCs we covered the importance of standardisation of characterisation parameters and definitions, with the inclusion of standard characterisation methods CV, GCD with appropriate analysis to avoid confusion. The efficiency, capacity, stability and cost of materials and processes need to be overcome before the commercial viability of PSCs is realised. We have seen some of these issues tackled by the reduction of device mass through two electrode configurations, reduction of material mass and volume and the use of more stable elements such as gel electrolyte and TMO based electrodes. Using existing fabrication techniques such as printing, and the creation of new fabrication techniques move us closer to achieving marketable products. By more fully understanding both the mechanisms of charge transfer and storage through novel in-situ techniques and material structure performance relationships, we can increase device efficiency further.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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The paper covers the main causes of inaccurate data reporting while showing examples of how researchers should report. They outline how best to measure and communicate the measurements of capacity, efficiencies and impedances they also discuss the differences of capacitive and pseudocapacitive materials. The supporting information includes an excellent checklist for reporting electrochemical storage data.

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The device uses a stable and low maintenance TMO heterojunction as harvest element and bridged to a porous stoneware tile base as a storage element incorporating Ni(OH)2-rGO-PPy composite pushing forward the ideal of a near-zero emissions building. The use of

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