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Supercapacitive biofuel cells

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Supercapacitive biofuel cells' (SBFCs) most recent advancements are herein disclosed. In conventional SBFCs the biocomponent is employed as the pseudocapacitive component, while in self-charging biodevices it also works as the biocatalyst. The performance of different types of SBFCs are summarized according to the categorization based on the biocatalyst employed: supercapacitive microbial fuel cells (s-MFCs), supercapacitive biophotovoltaics (SBPV) and supercapacitive enzymatic fuel cells (s-EFCs). SBFCs could be considered as promising 'alternative' energy devices (low-cost, environmentally friendly, and technically undemanding electric power sources etc.) being suitable for powering a new generation of miniaturized electronic applications.

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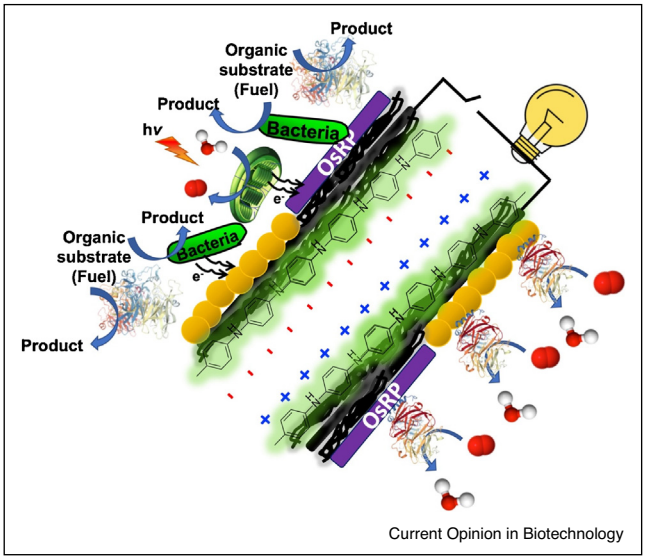
Introduction

SBFCs (supercapacitive biofuel cells) can be categorized as hybrid bioelectrochemical systems, where the electrodes perform a double function, notably the conversion of chemical energy into electrical energy (energy harvesting) and the storage of the electrical energy generated [1•,2]. The bio-conversion is usually carried out by electrodes modified with biocatalysts (e.g. bacterial or yeast cells, photoactive entities, enzymes etc.) that communicate with the electrode surface according to either direct or mediated (exploiting a diffusing/immobilised redox mediator that shuttles electrons) electron transfer pathways [3••,4–8]. Notably, the modified electrodes are connected to form a biofuel cell (BFC). In addition, the electrical energy generated in the BFC is stored in an electrochemical capacitor, also called supercapacitor. These days, electrochemical capacitors are designed using nanocomposites mostly based on carbon nanomaterials and metal nanoparticles, along with conducting polymers (e.g. polyaniline (PANI), polypyrrole (PPy) etc.) [9–11]. Notably, these devices are not able to produce electrical energy and hence need to be charged externally.

Recently SBFCs have been proposed as an alternative route to BFCs, which by themselves cannot produce a high and stable power output [12]. In contrast SBFCs are able to produce a stable and much higher power output (especially working in the pulsed mode) [13]. In this regard, the main advantage is the possibility to store the charge volumetrically rather than on an electrode surface, at a voltage difference specified by Nernst equation differently from an electric field applied considering the geometric constrains. In addition, SBFCs are fabricated by using renewable biological materials. SBFCs can be classified either based on their biological elements (e.g. bacterial cells, photoactive biosystems, enzymes etc.) and as conventional or self-charging/charge-storing BFCs. Based on the first classification, we can divide SBFCs in three main groups, namely supercapacitive microbial fuel cells (s-MFCs), supercapacitive biophotovoltaics (SBPV), and supercapacitive enzymatic fuel cells (s-EFCs), as schematically displayed in Figure 1. On the other hand, the classification is based on the ability of BFCs to work as conventional (producing low power and energy density) or as self-charging/charge-storing devices, also known as 'biosupercapacitors' able to produce a power output both during the charging and discharging steps. At this point, it is important to distinguish the abovementioned biosupercapacitors from the intrinsic self-charging devices, where the power output is produced only during the charging step.

In this review, we firstly aim at summarizing the most recent findings on SBFCs. We will discuss separately s-MFCs, SBPV and s-EFCs. In each section, we will highlight the advantages/drawbacks on using certain nanomaterials (e.g. carbon or metal-based nanomaterials, redox polymers, conductive polymers etc.) or a particular approach to develop supercapacitive devices also considering the possibility to be used not only as a source of renewable energy but also as self-powered biosensors as postulated in earlier reports.

Figure 1



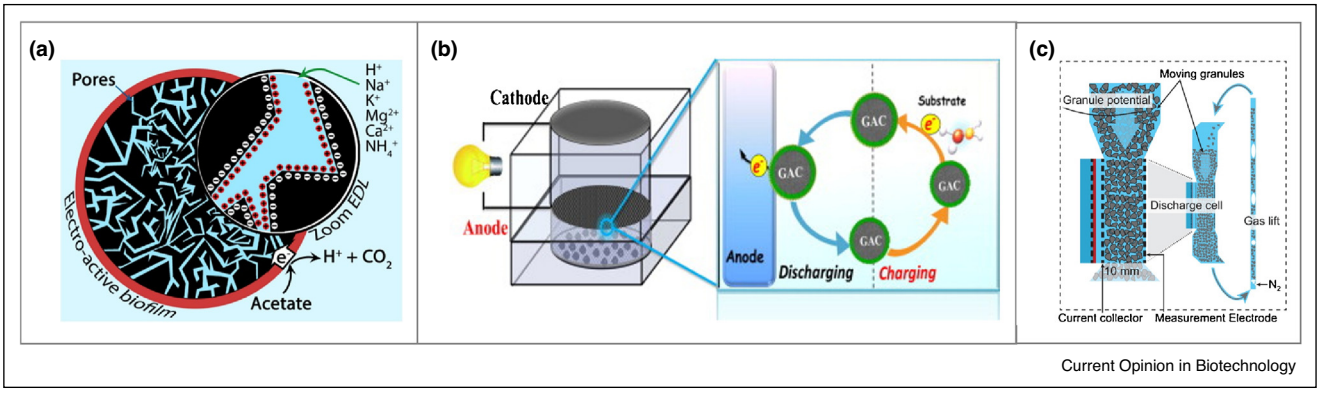
Schematic representation on the classification of SBFCs based on the bioelements present at the bioanode, where they can work either in direct or mediated electron transfer mode: supercapacitive microbial fuel cells (s-MFCs), supercapacitive biophotovoltaics (SBPV), and supercapacitive enzymatic fuel cells (s-EFCs).

Supercapacitive microbial fuel cells

Microbial fuel cells (MFCs) exploiting the capacitive feature of the electrode materials are denoted supercapacitive MFCs (s-MFCs). Such capacitive microbial electrodes were for the first time explored by Deeke *et al.* [14•] and received considerable attention in a number of research studies [15•,16]. The concept of a combination of MFCs with capacitors, both internal [17,18] and external [19,20], under charge-discharge conditions in comparison with conventional MFCs allows simultaneous energy harvesting and storage and enhanced current and power densities. Despite this, the desired level of power outputs is still a challenge in the microbe-based biosupercapacitors and is often limited by the performance of the anodes. In light of this, the capacitive anode materials have been subjected to extensive research in the past few years.

Conductive polymers, such as PANI or PPy, are widely used in MFCs to modify the bioanode, due to their low cost and large capacitance as an internal capacitive component. Such modifications allow a lower charge transfer resistance [21,22], a higher cumulative charge [23,24], and a power density production [21]. In recent works bioanodes employing PANI-based [25,26] and PPy-based [27,28] composites on various carbonaceous supports, such as activated carbon (AC), carbon brush, carbon nanotubes (CNTs), reduced graphene oxide, carbon felt, have been shown to be biocompatible, functioning as biocapacitors and enhancing the overall power density production of the tested MFCs. For instance, a MFC constructed of a carbon felt bioanode coated with a composite consisting of PPy-carboxymethyl cellulose-CNTs resulted in a maximum power density of 2970 mW/m^2, which is a 4.34 times increase in comparison to a MFC based on uncoated carbon felt bioanodes [28]. AC granules consitute another promising 3D high surface area electrode material used as capacitive bioanodes (Figure 2a) offering the separation of charge and discharge processes (Figure 2b) and improved the overall power output [29•]. The produced total charge was shown to be in direct correlation with the amount of biomass colonized on the granules, which is related to the available surface area [30]. The volumetric currents were affected and in an inverse relationship with the reactor or granule volumes, which is attributed to a good connection (i.e. a better granule-electrode physical contact and a longer retention time) between the granules and the final electron acceptor upon discharge action [29•,31]. The conduction of electrons between the granules and the electrodes was also determined by the exoelectrogenic bacteria having conductive *c*-type cytochromes in the outer membrane [32]. In light of this, the design of a reactor is a crucial factor in improving the capacitance discharge rate and further scaling up of such systems. Tejedor-Sanz *et al.* [30] showed that one-reactor system ensures a higher performance compared to a system with separated charging and discharging in the two reactors [33]. Implementation of a moving bed reactor (Figure 2c) allowed a longer contact time of the granules with the anode and resulted in a higher current density with a maximum of 23 A/m^2 [34]. Further improvements in the discharging of capacitive granules in a bed moving reactor was accomplished through increasing the potential difference and decreasing the distance between the granules and the current collector and increasing the bulk electrolyte conductivity [35]. The ratio between charging and discharging time is also an important factor in optimizing capacitive bioanodes [36,37]. Accordingly, applying a relatively short discharge (23 s) and a long charging (363 s) time, the moving bed was able to produce a current of 43 A/m^2 [37]. In parallel, efforts of scaling up various configurations of s-MFCs have been made by Santoro and co-workers. A self-stratified s-MFC operating in human urine with redox reactions occurring on both electrodes allowed for self-charging of the electrodes and a self-powering function [38]. The smaller (in carbon weight) the s-MFC in such systems, a higher power output can be expected, which implies thin-layered electrodes are more appreciated for supercapacitors [39]. Scaling of ceramic-based s-MFC by stacking 28 single MFCs, demonstrated a high power production under a supercapacitive operation mode [40]. A further improvement of the power generation of the s-MFC stuck was archived by introduction of a Fe-based catalyst for increasing the cathode potential [41]. The paper-based s-MFC took advantages of an easy-to-build and a low-cost design archiving a high power production [42].

Figure 2



(a) Schematized principle of functioning biofilm-carrying AC granules as capacitive bioanodes. The electroactive biofilm produces electrons via oxidation of a substrate, acetate (Faradaic reaction). The released electrons are stored at the highly developed pores in the carbon granules, while various cations are attracted to maintain the charge balance in the electric double layer, so the charge is stored (capacitive process). **(b)** Schematic overview of a fluidized capacitive reactor based on AC granules. The separation of charge and discharge processes takes place in a fluidized system, where granules can be charged via oxidation of a substrate and further discharged when in contact with a final current collector (anode). **(c)** A scheme of a moving granular bed. Reproduced and adapted from Refs. [31,49] and [37], respectively, by permission of Elsevier.

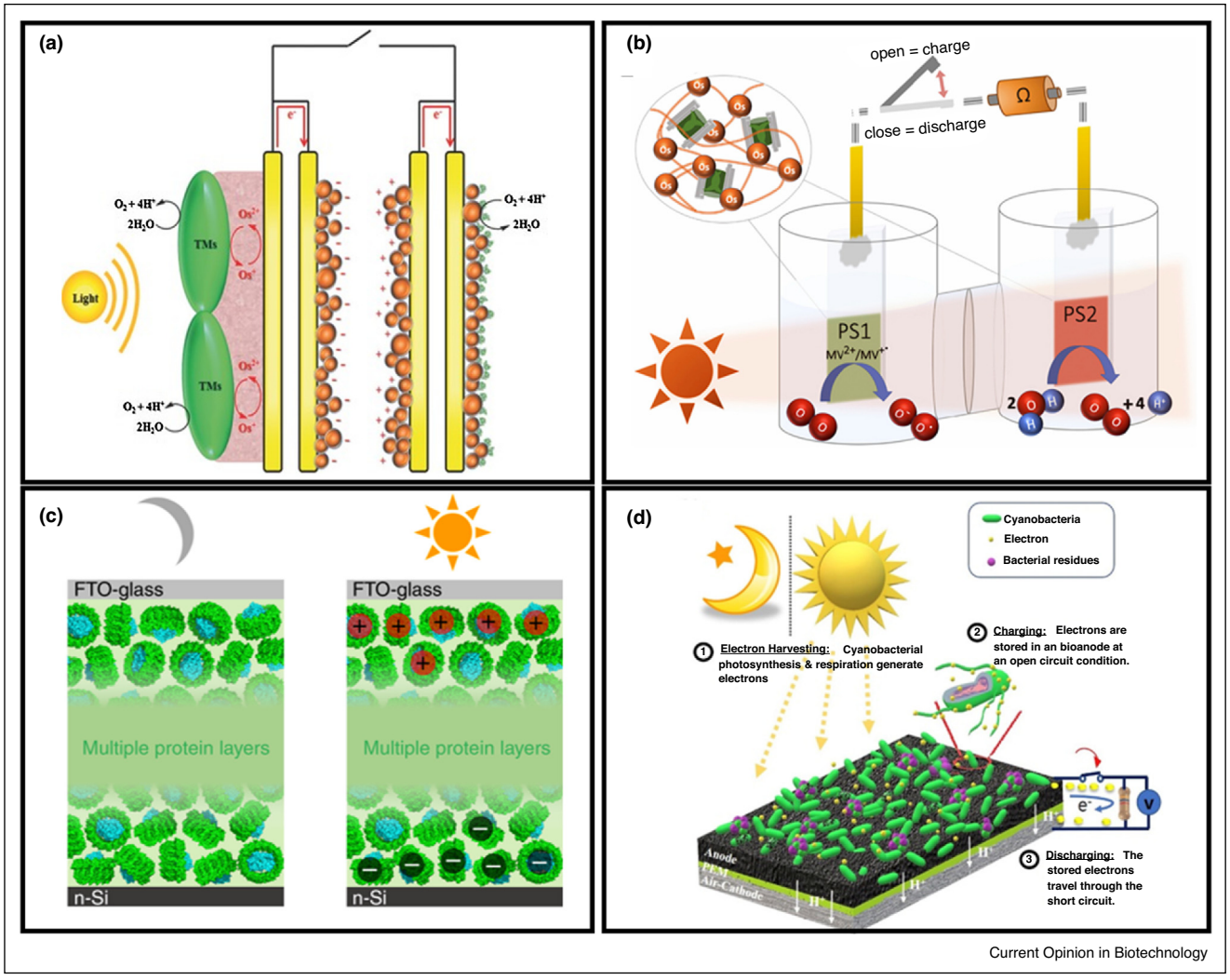
The application of highly porous structured materials is a common strategy in MFC technology not only for anodes, but also for cathodes. The overall performance of s-MFCs was reported to be improved by implementation of a carbon nanofiber composite [43], graphene nanosheets [44], or onion derived AC with an enriched content of nitrogen and phosphorous [45], which combine both the catalytic oxygen reduction activity and the electrochemical capacitive behavior of the cathodes. The use of double cathodes in combination with anodes of capacitive feature allowed to decrease the equivalent resistance and enhance the power output of the s-MFC [46].

A further improvement on the s-MFCs lays not only in the development of low-cost, high-capacitive and biocompatible electrode materials and development of easy-to-scale up designs, but also in the understanding of the mechanisms of electron storage in electroactive biofilms [47••] and to be able to manipulate the current generation and energy storage processes in bacteria [48••].

Supercapacitive biophotovoltaics

The initial attempts to investigate the influence of electrode capacitance on the photobioelectrochemical performance and to create a supercapacitive biophotovoltaic device (SBPV) with separated processes of solar energy conversion and electric power extraction were made by the Gorton group. A 2.5-fold rise in photocurrent density was demonstrated, when an additional inert electrode with an optimized capacitance was connected to the photobioanode (PBA) based on thylakoid membranes (TMs). TMs were immobilised within in the matrix of an Os-complex modified redox polymer (OsRP, poly(*N*-vinylimidazole)$_{10}$-Os(2,2′-bipyridine)$_2$Cl) acting simultaneously as a mediator to enable efficient charge transfer between the TMs and the conducting support (Figure 3a) [50•]. The SBPV assembled by combining a PBA with an enzymatic oxygen-reducing biocathode (bilirubin oxidase, BOx, immobilised on AuNPs) displayed a reasonable open circuit voltage (OCV) of ca. 0.4 V when charged under a light intensity of 400 W m^{-2}. A maximum power output of 2.6 μW cm^{-2} was registered at 0.15 V for the SBPV, which was 5 times higher than that for a BPV without supercapacitive electrodes. In a pulse self-charge/discharge mode, when the accumulated power was extracted from the fully charged device by applying constant current pulses, the power output was increased up to 56 μW cm^{-2} with a residual stability of 60% after 6 hours of continuous insolation. Furthermore, several SPBVs have been realized by immobilizing TMs onto indium tin oxide (ITO) [51] or multiwalled CNTs [52] electrodes (DET process). Utilization of positively charged amidated CNTs as a support for the immobilization of TMs resulted in a 1.5-fold enhancement of the photocurrent density compared to that for the PBAs based on negatively charged carboxylated CNTs. The maximum power output achieved for a mediator-less SBPV in continuous mode was 0.66 μW cm^{-2} (0.21 V, 400 W m^{-2}), which could be increased by more than two orders of magnitude in a self-charge/discharge regime. For example, CNTs with a different surface carbon to oxygen (C/O) ratio resulted in affecting the performance of the PBA, where TMs were connected in MET through an OsRP. In particular, CNTs with a higher C/O ratio exhibited a higher maximum photocurrent density and with a reduced charge transfer resistance [53], regardless the fact that the CNTs were covered with a layer of OsRP and the TMs were not directly connected to the CNT surface.

Figure 3



Schematic representations of **(a)** a mediated TM-based SBPV, **(b)** a light-driven Nernstian biosupercapacitor, **(c)** a charge-storing biophotonic power cell based on an isolated bacterial protein complex, and **(d)** a self-charging cyanobacterial supercapacitor. Adapted with permission from Refs. [50•,54,57••,58].

Zhao *et al.* developed a so-called Nernstian biosupercapacitor (Figure 3b) [54], where electric charges generated due to the photocatalytic activity of isolated photosystem 2 and photosystem 1 protein complexes were accumulated in the form of oxidized/reduced moieties in the matrix of an OsRP (poly(1-vinylimidazole-co-allylamine)-Os(2,2′-bipyridine)$_2$Cl). The same OsRP was used in both photosystem 2-based PBA and photosystem 1-based PBFC using a porous ITO support. Starting from the initial OCP of ca. 0.41 V versus SHE, corresponding to equal activities of Os^{2+} and Os^{3+}, the potentials of the PBA and the photobiocathode changed to 0.29 V and 0.465 V, respectively, after 200 s of irradiation (red light, 6.5 mW cm^{-2}). This corresponds to an OCV value of 0.175 V, which is 2.5-fold lower compared to those analogous bioelectrochemical systems, where oxygen-reducing and glucose-oxidizing enzymes were used as biocatalysts [55,56]. The power output extracted from the fully charged device by applying a load of 50 kΩ was 1 μW cm^{-2} and decreased to 0.54 mW cm^{-2} after 15 consecutive charge/discharge cycles.

The approach of using the same biomaterial for light energy conversion and charge storage was proposed by Ravi *et al.* [57••]. A multilayer film of concentrated PufX-deficient RC-light harvesting 1 complex from *Rhodobacter sphaeroides* (RC-LH1) was sandwiched between a fluorine-doped tin oxide electrode and an n-doped silicon electrode enabling a light-driven net oxidation and reduction of the RC-LH1 proteins, respectively (Figure 3c).

The maximum OCV for the SBPV self-charged under 1 Sun illumination was ca. 0.4 V, which is close to the predicted maximum for a Nernstian system consisting of surface-confined redox species [55].

The first example of a cellular microbial SBPV was presented by Liu and Choi (Figure 3d) [58]. The microliter-scale device was comprised of an oxygen reducing Pt-based cathode and a PBA, where the photosynthetic reactions of a biofilm composed of *Synechocystis* sp. PCC 6803 cyanobacteria were used for charge generation. The PBA was based on carbon cloth fibers covered with a layer of poly(3,4-ethylene dioxythiophene):polystyrene sulfonate (PEDOT:PSS) to improve the surface affinity of the cells and an increased charge-storing ability of the PBA. The OCV of the fully charged device achieved after 28 min of illumination under a non-specified light intensity was in the range of 0.21−0.23 V, which was multiplied to 1.8 V by combining eight separate SBPVs in series. Maximum power and current density of the assembled 8-unit device were 38 $\mu W\ cm^{-2}$ and 120 $\mu A\ cm^{-2}$ obtained by applying an external load of 10 kΩ with *ca.* 10% of OCV degradation after 18 hours of continuous operation by 28 min of self-charging and 2 min of discharging. Apart from the obvious novelty of utilization of whole cells in the SBPV, the authors highlighted the influence of the discharge current on the long-term stability of the PBA, when both an overstated and understated resistance of the applied load resulted in a relatively fast degradation. Despite the advances achieved by intermittent extraction of accumulated charges, the performance in continuous mode displays a low maximum power output of 0.5 $\mu W\ cm^{-2}$ (at *ca.* 0.03 V) for a single-unit SBPV.

The energy converting performance was further improved by introducing a mixture of CNTs and MnO_2 to the PEDOT:PSS capacitive layer [59]. The OCV value was increased up to 0.47 V, the maximum power density in continuous mode was 25.3 $\mu W\ cm^{-2}$. However, the photocatalytic output from the CNTs and MnO_2 was not extracted from the presented data and these values cannot be fully representative for the cyanobacterial (photo)bioelectrocatalytic activity.

Supercapacitive enzymatic fuel cells

The first supercapacitive enzymatic fuel cell (s-EFC) was described by Shleev's group based on the idea of combining double-function electrodes into a self-charging biofuel cell [60••]. In particular, the electrochemical electromotive force driving the charging process was generated by combining double-faced electrodes modified with a glucose-oxidizing enzyme, cellobiose dehydrogenase (CDH, anode), and an electrode modified with BOx as cathode [13]. In addition, the other electrode face was configured to store the charge, based on a PANI/CNT composite, as shown in Figure 4a. This device released a power output of 1.2 $mW\ cm^{-2}$ at 0.38 V, notably 170 times higher than the result for the enzymatic fuel cell by itself [1•]. At the same time, Cosnier's group demonstrated the fabrication of a double layer biosupercapacitor including redox enzymes for continuous charging (Figure 4b) [61].

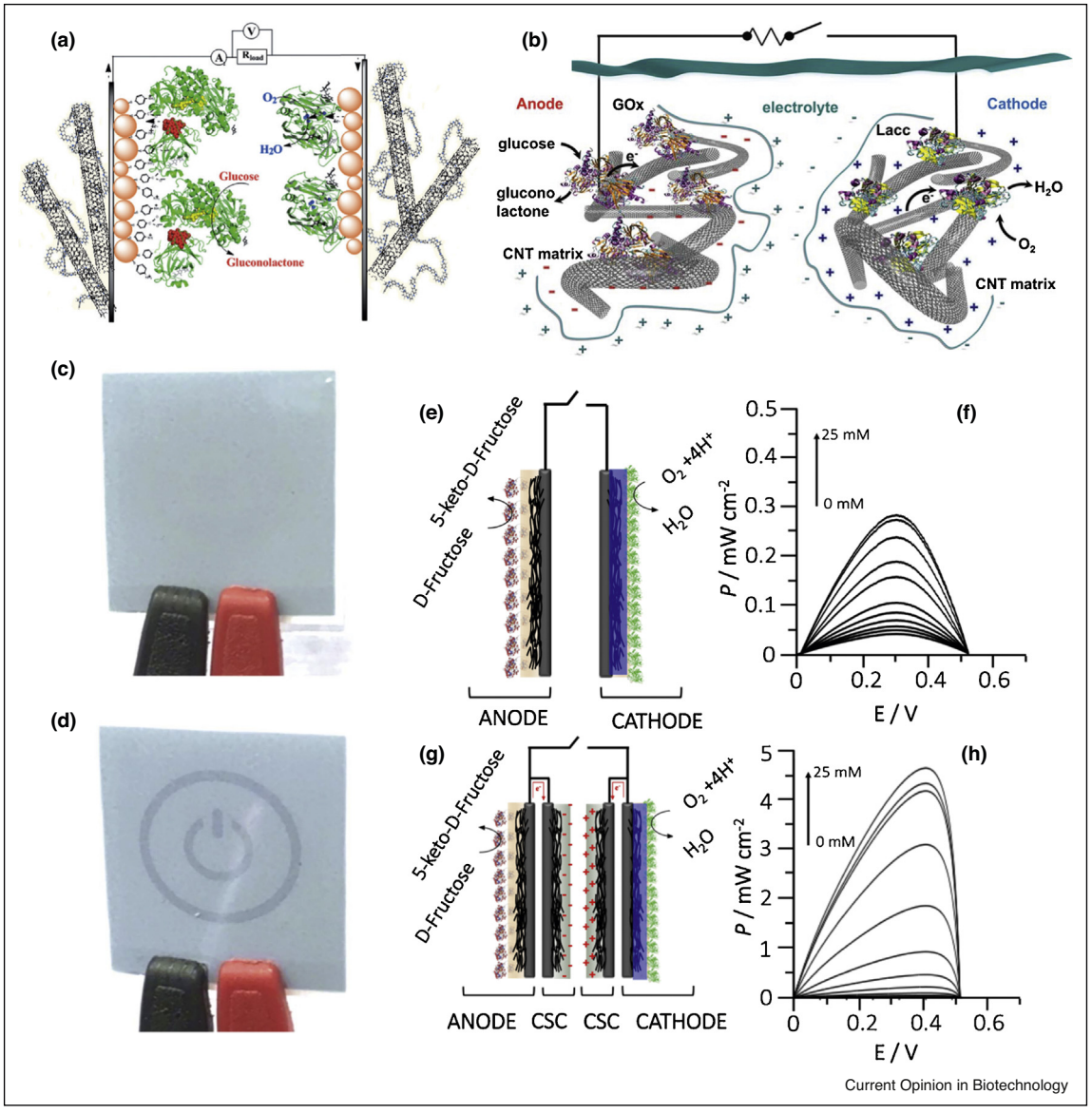
Later, a device based on the deposition of the same OsRP on both the CDH anode and the BOx cathode has been proposed in order to demonstrate that the self-charging process initiates only in the presence of the biofuel leading to an OCV of 0.45 V. After charging, the biodevice was able to produce eight times the power output released in steady state conditions [55].

In the past six years, several s-EFCs regarded also as biosupercapacitors have been proposed [1•]. In 2015 Kizling *et al.* reported on a biodevice based on a bioanode modified with a cellulose/polypyrrole composite and fructose dehydrogenase (FDH). This bioanode was combined with a biocathode based on naphthylated CNTs with adsorbed laccase (Lc), producing 1.6 $mW\ cm^{-2}$ at 0.33 V on transient basis [62]. Furthermore, several s-EFCs were combined in series in order to be able to power an oxygen sensing electrode. This configuration has been recently reported with an enzymatic cascade in order to produce a sucrose fuelled s-EFC [63].

In a similar approach, in 2016 Villarrubia *et al.* proposed an integrated fuel cell/supercapacitor wherein fuel is delivered by a paper-based microfluidic system. Indeed, the novelty here is the combination of a capacitive bioanode based on buckypaper modified with methylene green and NAD^+-dependent glucose dehydrogenase (GDH) with an air breathing BOx cathode. The biodevice could provide 0.87 $mW\ cm^{-2}$ at 0.56 V during 0.01 s pulses, 10 × higher than achievable steady-state parameters [64].

Alternatively, a glucose/O_2 SEFC based on FAD-dependent GDH and BOx has been realized releasing a power output density of of 3.0 ± 0.5 $mW\ cm^{-2}$ [65]. In 2017, Xiao *et al.* developed a biodevice meant to work as an autonomous pulse generator, generating a peak power density of 0.61 $mW\ cm^{-2}$ at 0.4 V under pulsed operation (notably a 470 times higher value than what was achievable under steady state conditions) [56]. In a similar configuration, the authors replaced the BOx modified biocathode with an MnO_2 modified electrode that would be oxygen insensitive [66•]. This device could be considered a promising approach to develop implanted s-EFCs, where the limited concentration of O_2 could affect the performance of a s-EFC. In 2018, Bobrowski *et al.* realized a flexible s-EFC based on an ITO transparent support modified with a spray of ITO nanoparticles to provide a porous surface (increasing the enzyme load) as displayed in Figure 4c and d [67]. The s-EFC generated a power output of 0.030 $mW\ cm^{-2}$ at 50 μM glucose (approximately the glucose concentration in human tears) in a discontinuous charge/discharge mode, which is 350 times

Figure 4



(a) Schematic representation of the first SEFCs based on a CDH-AuNPs modified bioanode combined with a CNTs-PANI composite and a biocathode modified with BOx-AuNPs/CNTs-PANI; **(b)** Scheme of the electrochemical double layer supercapacitor/biofuel cell hybrid system; Flexible s-EFC in OFF state **(c)** and ON state **(d)**; **(e)** Schematic representation of an FDH-Lc based EFC; **(f)** Power output profiles recorded for the FDH-Lc EFC in 50 mM NaAc buffer at pH 5 containing different concentrations of D-fructose from 0 mM up to 25 mM and in equilibrium with air (source of O_2). The plot was obtained from linear sweep voltammetry at 1 mV s^{-1}; **(g)** Schematic representation of an FDH-Lc s-EFC; **(h)** Power output profiles recorded for this s-EFC in 50 mM NaAc buffer, pH 5 containing different concentrations of D-fructose. (a) reproduced from Ref. [60••] with permission of Wiley. (b) adapted from Ref. [61] with permission of RSC. (c) and (d) reproduced from Ref. [67] with permission of Elsevier. (e)–(h) adapted from Ref. [74••] with permission of Elsevier.

higher than the power density released from EFC operating in continuous mode. In 2018, Pankratov *et al.* presented a fuel-independent self-charging s-EFC, by exploiting the supercapacitive properties of myoglobin possibly replacing a fuel-dependant bioanode [68]. Successively, the same authors realized the very first example of an s-EFC, where the charge-storing function was performed by cytochrome *c* on both electrodes. The biodevice could provide 4.5 μW cm^{-2} of power output in pulsed mode (notably 15 times higher than that under steady-state conditions) [69]. In the same year, Alsaoub *et al.* reported on the development of an intrinsic s-EFC based on a high-potential bioanode and a low-potential biocathode [70••]. This EFC conformation in a discharge

mode would not produce any OCV or power output. After charging, a Nernstian shift (phenomenon previously reported for pseudocapacitive electrodes) [71] occurred at both elements lifting the OCV to approximately 0.4 V. The presented concept demonstrates that, for the design of new s-EFCs, the conventional design criteria of BFCs do not necessarily hold and that despite an apparent potential mismatch between the redox polymer and the enzyme, intrinsic s-EFC provides a sufficient voltage output [72].

Recently, s-EFCs have been proposed as self-powered biosensors [73]. In this regard, Bollella *et al.* reported on a combination of an FDH-anode and a Lc-cathode, and charge-storing electrodes based on PANI/multiwalled carbon nanotube nanocomposites (Figure 4e–h) [74••]. The device was working according to a two-step process, notably the charging and sensing steps. This idea has been previously proposed considering pulses constant application. The proposed s-EFC showed excellent biosensing features in terms of sensitivity (3.82 ± 0.01 mW cm^{-2} mM^{-1}) and operational stability (retaining up to 90% of its initial power density after 8 hours of continuous operation). This approach has been alternatively exploited to develop an s-EFC for the detection of glucose as a potential implanted device [75].

Conclusion and outlook

Till now all possible types of SBFCs have been already realized by exploiting different biosystems like microbial cells, photoactive biosystems and enzymes. In the last six years, pseudo, double-layer and hybrid biodevices were designed and tested. The devices herein reported can be considered as early scientific prototypes rather than practically useful energy sources, mainly due to their operation in low-voltage and low-current regimes. However, because of the limitations of the biological material used and the electrode sizes SBFCs will not be able to compete with devices based on inorganic and organic materials. Nevertheless, these devices are important from the fundamental point of view allowing for the investigation of electron transfer processes between different biocatalysts and electrode surfaces [1•,73]. For example, certain self-charging biodevices like SBPVs can be practically used, especially considering that solar energy is intermittent in Nature, hence allowing to store the electricity generated. However, we believe that an increased understanding of the fundamentals of biological electron transfer mechanisms in bacteria and in photosynthetic systems and between such systems and electrodes in combination with the rapid development in conducting nanomaterials [3••,6,76–80] will pave the way for a further rapid development in this area.

Conflict of interest statement

Nothing declared.

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