Water-Enabled Electricity Generation: A Perspective

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1. Introduction

Two critical issues now facing human society are the global dependence on fossil fuels and the impact of fossil fuels on the environment.[1–5] The increasing utilization of fossil fuel energy represents a continuing threat to global warming, which now is realized as the biggest challenge for the sustainable development of human life. To address these issues, scientists have devoted extensive efforts to developing advanced technologies involving renewable and sustainable energy sources, with the aim of replacing traditional fossil fuels.[6] In this regard, a variety of novel energy harvesting technologies based on triboelectric,[7] piezoelectric,[8] and thermoelectric principles[9] have been evaluated for the conversion of green energy to electricity. Recently, the vast reservoir of low-grade energy from water/moisture in the earth’s atmosphere has attracted great interest in energy-conversion technologies.[10–16] The atmosphere has long been recognized as a sink of electrical power, as water covers ≈71% of the earth’s surface, and water vapor or moisture is abundant almost everywhere. Despite the ubiquitous presence of water, opportunities for water-enabled electricity generation has been usually overlooked.[17,18] The possibilities for electricity generation are facilitated by the electrification of water in response to changes in phase but experiments directed toward the harvesting of this charge to generate electrical power from atmospheric water vapor have been only recently been reported.[11,15]

Since graphene oxide (GO) can generate electricity when exposed to moisture, this material has attracted much attention as a power source in a variety of practical applications.[19–24] Other materials evaluated for use for water-enabled electricity generation include carbon nanoparticles (CNP),[23] bio-fibers,[26] metal–oxide nanowires,[10] and a variety of 2D materials.[21,27]
The generation of electricity in these devices derives from the nature of the water–solid interaction, and is mainly based on either ion diffusion or the presence of a streaming current as water flows or diffuses in the active material. The surface status of the active materials plays a vital role during the electricity generation of streaming current, as the surface charge of the nanoparticles decides the polarity and the specific value of the power generated. In contrast, it usually needs to be hydrophilic to realize an effective interaction between the water molecules and nanomaterials, like the surface charge generation, water flowing through a nanochannel, dissociation of functional groups. A high surface area can provide abundant sites for these processes as well, which can facilitate power generation.

The electrical output of a moisture-enabled electricity generator can be in the form of voltage/current pulses or continuous DC output, while the time duration of this output depends on many factors and can range from milliseconds (ms) to several days. The development of new nanofabrication techniques and the exploration of new materials together with materials design have enabled increases in output voltage from the millivolt range to several volts. Recent improvements in technology have extended this voltage range to 1 kV, and provided enough electrical power to run common electronic devices. An important aspect of these green energy sources is the ease with which they can be used for applications in self-powered devices (Figure 1). This has led to the incorporation of water-enabled electrical generators (WEEGs) in novel self-powered, battery-free electronic and monitoring/diagnostic systems in health care, the internet of things (IoTs), the environment, security and information applications, and artificial intelligence. There is no doubt that additional practical applications for WEEGs in these and other scenarios will boost the development of user-friendly, environmentally sustainable devices.

In this article, we focus on the development of the WEEGs, suggest the remained challenges and future opportunities. We discuss the two basic mechanisms of energy conversion induced from ambient moisture from the perspective that WEEGs provide a new paradigm for battery-free power in a variety of applications that may benefit humanity. In this context, recent advances in the characterization and performance of materials for WEEG applications are summarized. In addition, recent material and fabrication techniques that circumvent bottlenecks in increasing electrical output are discussed. Finally, we address some opportunities and challenges in both materials design and practical applications for WEEGs.

2. Mechanisms

The interactions between water molecules in liquids and gases and nanoscale and microscale materials play a key role in water-enabled electricity generation. It has been reported that the electrical power can be generated in these systems via a variety of physical mechanisms including electron drag, the coupling of ionic motion to surface charges, through interface charging/discharging cycles, water splitting, photothermal effect, and the establishment of a streaming potential. Chemical mechanisms such as the diffusion of ions in response to a gradient in concentration and redox reactions have also been evaluated as a means of harvesting energy in the WEEG configuration.

From the aspect of external stimuli, droplet-based, waving or shaking water-induced, water-flow-induced and phase-change-based WEEGs are mainly classified. The water-droplet-based electricity generation tends to be transient resulting from a limited time duration of reaction and the time duration of output signals is usually about several seconds. It includes the wasted mechanical energy harvesting from charging–discharging of pseudocapacitor from a sliding droplet or intermittent raining droplets as well as the streaming current. The wasted kinetic energy from water waves or shaking water can also be harvested by electrical double layer (EDL) moving effect, work-function-based tuning mechanism, or capacitance variation process. The output signals are pulses-like because of the action characteristics of water, but the process can be repeated frequently unless there is materials collapse occurs. For a water flow stimulated by water evaporation, the thermal energy is harvested through the generation of streaming current and the DC signal can be maintained for hours or even days as long as the nanostructured materials are maintained well. The phase change process of water along with moisture absorption and desorption lays another foundation for energy harvesting from chemical potential energy. The process can be intermittent with fast moisture absorption and desorption. With an improved nanostructured material, continuous DC signals can be maintained for days.

As this electricity generation technique has been focused only very recently, the detailed interpretation for the mechanisms is still under some debate. Of these several possibilities, the
production of electricity by harnessing the streaming current, as well as protocols associated with the diffusion of ions in a concentration gradient, are currently favored as they are relatively simple to implement and are capable of generating high output power.[12,23,38,45] The fundamental physical processes involved in power generation in streaming and ionic flow devices are illustrated in Figure 2.

**Figure 2.** Schematic illustrating the principles involved in each mechanism for generating electricity: a) Distribution of charges in the nanochannel when exposing the nanomaterials to moisture. b) A process dominated by the streaming current. c) A functionalized surface containing a gradient in surface functional groups. d) Voltage generation in a system with a gradient in surface functional groups produces a gradient in proton concentration.

### 2.1. Streaming Current/Potential

Streaming current or streaming potential originates when liquid moves through a porous structure or micro-/nanochannels with charged walls, inducing the migration of free charges generated at the water–solid interface.[49,50] This phenomenon has been known for over a century. Most solids develop a surface charge from the ionization or dissociation of surface groups, adsorption of ions from solution, or the substitution of surface ions when in contact with water or other liquids.[51] An equal but oppositely charged region of counterions is developed in the liquid outside the solid particle to balance this charge, forming a Stern layer consisting of immobile ions and an outer diffusion layer containing mobile ions as shown in Figure 2a. An EDL is formed at the surface and consists of this mixture of charges bonded to the surface and free charges in the liquid over the surface. The characteristic dimension of the EDL is the Debye length, which depends on the nature and concentration of ions in solution over the surface. In a porous medium, the critical parameter is the ratio of the Debye length to the channel diameter, $D$, as high electrical output is only obtained when the EDLs on each side of a channel overlap.[50] Under these conditions, mobile counterions exist in the center of the channel. These mobile charges in the water within the EDL move under an external pressure or capillary force, resulting in an electric current (i.e., the streaming current) along the channel. This process is illustrated in Figure 2b. The streaming current, $I_s$, is known as the streaming potential:[50]

$$I_s = \frac{A \varepsilon_0 \varepsilon_r \Delta P \zeta}{\eta l}$$

where $A$ is the total cross-section of the pores, $\varepsilon_r$ is the dielectric constant of water, $\varepsilon_0$ is the electrical permittivity of vacuum, $\eta$ is the viscosity of the solution, $l$ is the pore length, $\Delta P$ is the pressure difference, and $\zeta$ is the zeta potential.

The accumulation of counterions at the downstream end of the channel leads to a potential difference, $V_s$, known as the streaming potential:[50]

$$V_s = \frac{\varepsilon_0 \varepsilon_r \Delta P \zeta}{\sigma \eta}$$

where $\sigma$ is the electrical conductivity of the solution.

Apparently, the energy that causes the flow or diffusion of water molecules can be harvested and converted into electricity this way. Compared to the bulk materials with large channels where the mechanical energy is used to flow water, the nanomaterials can harvest thermal energy from the ambient environment through the natural water evaporation process. Xue et al. first demonstrated that water molecules spontaneously flow along the charged nanochannels formed by CNPs during the natural evaporation process.[16] Both voltage and current output will be maintained until all the water is evaporated completely. The role of water evaporation in electricity generation was confirmed by the vanish of output when the evaporation process was stopped by sealing the system. The energy conversion efficiency can be calculated by taking the ratio of the electricity energy output and the total thermal energy difference of water from liquid to vapor, supposing that the specific energy difference is 2.26 kJ g$^{-1}$.[17] Other forms of energy such as solar energy can also be harvested through the water evaporation process with the help of the photothermal effect.[52]

From the aspect of active materials, both the streaming current and the streaming potential can be optimized by tuning the zeta potential and the pressure difference applied along the channel.[53,54] The streaming current can also be enhanced with a larger contact area and smaller pore length. A high voltage output
can be obtained with enhanced charge density, which lays the basics for performance optimization especially for water-droplet-based WEEGs.[12]

### 2.2. Ionic Diffusion

The extraction of energy from changes in the chemical potential of water can occur when the materials in the moist electricity generator (MEG) are electrophilic and contain an abundance of surface groups such as –OH, –COOH, –COONa, and –SO3H.[23,30,31,38,39] The absorption of water molecules from ambient moisture on these materials then leads to the dissociation of surface functional groups and the release of a high density of mobile ions, e.g., protons. With the introduction of water, the water molecules and associated protons migrate subject to the gradient in concentration. This migration then generates an electrical current. In practice, this process occurs when water is introduced through an electrode on one side with a porous nanostructure producing a gradient in the concentration of water molecules inside the porous layer.[18,35] The highest voltage reported for a generator of this type is typically ≈0.7 V.[35] It is apparent that as the ionization or dissociation of surface functional groups leads to a negatively charged surface and the release of protons that are incorporated in the diffusive flow, the electrical output derives from a streaming current as in the previous mechanism.

Higher output power can be generated by fabricating the active layer such that it presents a heterogeneous chemical structure as shown in Figure 2c, while allowing the moisture to randomly flow into the system.[15,39,44–46] When GO is the active layer, a gradient in the distribution of the functional groups can be introduced through a partial reduction of the graphene oxide (rGO) by moisture-electric annealing (MeA).[15,39,44] Asymmetric heating by a hot plate,[46] or by laser processing on one surface of the active layer.[45] On exposure to water, a gradient appears in the concentration of protons released from the functionalized surface. These protons diffuse in response to the concentration gradient while the surface groups are immobile. This flow results in the generation of an electric field and the appearance of a voltage difference between the external electrodes. A schematic representation of this process is shown in Figure 2d. It has been found that the open-circuit voltage can reach 1.5 V when the system is exposed to an atmosphere at 80% relative humidity (RH) at 25 °C.[45]

A natural question on the MEGs based on this mode is whether the electricity generation is related to redox reactions with systems composed of different metals working like Volta batteries. In most reports, redox reactions of metals with water seem to be excluded from electricity generation as inert metals such as gold are usually used as electrodes.[15,30,31] Huang et al. compared the output of devices with both electrodes made from the same inert materials and shows that Au, Pt, and graphite have little effect on the output characteristics.[31] Both active materials and electrodes employed show no apparent chemical and morphological difference before and after the moisture is applied, which also excludes the chemical reaction process.

Due to the limited capacity of ions generated from the interaction between water and active materials, the output electricity cannot be maintained infinitely. The electricity generation process will stop when the water adsorption tends to be saturated, unless the water adsorption ability is recovered by removing the absorbed water from active materials. The early MEGs usually work in a cyclic pulse mode as the electricity generation only lasts for seconds,[15,45] while the recent MEGs can work in a relatively continuous mode and the output can be maintained from tens to hundreds of hours before it decays.[30,31] In the process of water adsorption, the variation of the chemical potential energy of water molecules from gaseous water in the air to adsorbed water in active materials could be the main energy source for electricity generation (Figure 3). By measuring the output energy and calculating the Gibbs free energy variation of water molecules from a free gaseous state to an adsorbed state, Huang et al.[31] and Zhao et al.[47] reported the energy conversion efficiency of ≈1% at 298 K under constant RH of 25% and ≈51% at cyclic RH of 80%, respectively.

Since the gradient-driven diffusion of ions dominates in the generation of electrical power, the overall electrical output can be influenced by changes in temperature, RH, and the difference in the concentration of ions. All of these factors can be used to adjust the electrical power output of these devices.[30,38]

### 2.3. Other Energy Conversion Technologies and Mechanisms Based on Water

In addition to the aforementioned two basic mechanisms that cause the water-enabled electricity generation, some other water-based physical processes such as water splitting[56–58] and photothermal effect[59–63] also have been used to harvest energy based on water (Figure 4). Figure 4a shows energy harvesting atmospheric humidity from ferroelectric-semiconductor photoanode (BaTiO3@BiVO4) that can perform efficient water oxidation when the moisture from the atmosphere is collected by the super-hygroscopic hydrogel. The hydrogel has a high water absorption capability (>400%), enabling the abundant hydrogen supply for continuous water-to-H2 conversion. As water molecules are absorbed, the hydrogel acts as a dehumidifying agent and carries water to the photoanode for power generation, being connected in series with a solar cell, further boosting the carrier’s mobility.[56,58] This intelligent system can generate a photocurrent of 0.4 mA cm−2 with a relative humidity reduction of 12.0 % under an illumination of 10 mW cm−2.[56,58] Here, the solar energy is converted into electricity, with water oxidized into H2 and O2 that can also be collected as clean fuel.

Figure 4b shows the thermolectric unit with a temperature gradient from hot and cold ends caused by the water steam generation through carbonized materials under solar light irradiation. The heat from solar irradiation is localized at the top of the surface acting as a hot end and water-bearing sponge that draws the water up plays the role of creating a cold end for thermal electricity generation. A temperature difference of ≈8 °C can be achieved under 1 sun irradiation, inducing an open-circuit voltage of 95 mV and short-circuit current as high as 17 mA.[59] The power output of the generator under 1 sun is about 0.36 mW for each 3 × 3 cm thermolectric unit, nearly 14 times that of the control tests using thermolectric unit only.
(0.026 mW). In this configuration, the water acts as the temperature gradient medium under light irradiation, enabling electricity generation from thermoelectric units. The photothermal effect can also be used to assist the flow of water from low salinity end to high salinity end, with simultaneous steam generation under the solar irradiation as shown in Figure 4c. Similar to the streaming current/potential process described in Figure 2, the water will interact with CNPs and generate electricity output during the flow of the water molecules through the charged nanochannels formed by nanoparticles. An open-circuit voltage of 0.2 V can be obtained in this way.

3. Electricity Generation Characteristics

The temporal output of a water-enabled electricity nanogenerator depends on the nature of the interaction between incident water molecules and the active layer fabricated from nanomaterials. In practice, the time-dependent output of this type of generator will depend on the availability of water. When water is introduced intermittently in the form of droplets then the electrical output generally appears as one or more individual pulses. Obtaining a continuous DC output from a WEEG based on a streaming current requires a continuous flow of water or moisture through nanochannels whose surface chemistry is unaffected by sustained exposure to water.\(^\text{[16,25,53,64–66]}\) An example of such a system using a porous carbon black (CB) sheet as the active medium is shown in Figure 5a,b. This device is capable of generating \(\approx 1\) V for more than 160 h when subjected to evaporative flow in an ambient environment as illustrated in Figure 5a.\(^\text{[16]}\) When operating with water droplets, WEEGs tend to generate pulsed output signals as the voltage is produced only when a limited quantity of water passes through the nanochannels in the active medium.\(^\text{[12–14]}\) For example, dropping 8 μL of water on a porous Al₂O₃ layer yields voltage pulses that only persist for 2–3 s (Figure 5d,e).\(^\text{[12]}\) The rise time for the initial response to water in this device was found to be tens of microseconds. Other WEEGs operating with water droplets have response times of 10 ms (Mg-carbon nanofiber (CNF) active medium) and 244 μs (TiO₂-CNF active medium).\(^\text{[13,14]}\) It has been found that this type of WEEG can be used as water sensors or water detectors.

In the case of WEEGs based on the flow of ions in a concentration gradient, the voltage output can be either transient or continuous, depending on the composition and morphology of the active medium and the way moisture enters the system. For most generators, the voltage signal only lasts for tens of seconds since the space density of ions liberated from the surface of the active medium is limited and these are swept away to be desorbed from the system (Figure 6a–c).\(^\text{[48]}\) This performance can be greatly improved by designing the active medium to exhibit a high uptake when exposed to water and high ionic conductivity in the surface nanostructure.\(^\text{[10,38]}\) The electrical output of such optimized structures can continue for days. The active medium of the device shown in Figure 6d is a mixture of GO and sodium polyacrylate (PAAS). The nanochannels in this structure have a high aspect ratio and contain surface groups that are highly
hydrophilic. These properties combine to facilitate a high moisture uptake, enabling the spontaneous absorption of water molecules from the atmosphere, and the directional diffusion of ions released from the surface. This device delivers a DC output for more than 120 h in a humid ambient environment. A similar generator, consisting of a protein nanowire film containing a broad distribution of nanopores, has been engineered to produce a self-maintained moisture gradient within the film and has been found to give a DC voltage output of ≈0.5 V for more than two months in an ambient environment with fluctuating humidity (Figure 6e,f).

4. Materials

Nanomaterials including 0D nanoparticles, 1D nanowires, 2D thin films and 3D foams, with a high surface area to volume ratio and extensive reaction sites, are ideal as the active medium in water-enabled electricity generators. As a result, many functional materials including carbon-based materials, solid oxides, biomaterials, and composite systems have been used in WEEGs in order to improve output performance. A summary of the output characteristics of some of these devices under standard operating conditions is shown in Figure 7. Because carbon-based materials have a high conversion efficiency, they account for the majority of the active materials used in water-enabled electricity generation systems, with the focus being on graphene-based materials, CNPs and carbon nanofibers (CNFs), polymers, and biomaterials. Solid oxide materials are also favored as they are easily fabricated into an active layer and are stable even in harsh environments. Some other materials suitable for applications in WEEGs include Mg, Si, Ni-Al, Cu-Zn, and glass fibers. With the development of techniques for the synthesis and fabrication of these materials, the voltage output of a single WEEG has now been improved substantially from millivolts to in excess of several volts (Figure 7b–d) in the past seven years. Now that the voltage output of integrated devices can be as high as 1000 V, it is evident that these generators are widely applicable in a variety of applications.

4.1. Carbon-Based Materials

Carbon-based materials have a range of physical, chemical, and electronic properties that make them attractive as active media in
In this context, GQDs, GO, CNPs, carbon nanotubes, various types of polymers (PSSA, PAAS, poly(vinyl alcohol)-PVA) and biomaterials (protein nanowires, natural wood, paper) have been evaluated for applications in WEEGs. A primary advantage of these materials is that they are strongly hydrophilic, which facilitates the absorption of water molecules from moisture or liquid water. They can also be prepared with a high specific surface area, which provides the high density of reaction sites containing oxygenated functionalities necessary for the release of ions into the liquid in contact with the surface.

4.1.1. Graphene-Based Materials

Atomically thick graphene exhibits an excellent combination of electronic and thermal conductivities, extreme mechanical strength, and large specific area. It can also be modified to contain a high density of oxygen-bearing functional groups including –OH and –COOH. These groups efficiently absorb water molecules when exposed to moist air or liquid water promoting a reaction that releases protons into the ambient environment. These protons are mobile and migrate in solution under a gradient in moisture, or subject to the ion gradient originating from an asymmetric concentration of functional groups. While the output voltage is often small, graphene-based WEEGs deliver high power density as shown in Figure 7b. In a system based on GQD, a power density of 1.86 mW cm$^{-2}$ was obtained under a 70% RH variation.

As seen in Figure 7a, GO is the most widely used material for WEEGs in current applications. For example, 1D GO fiber generator acts as a wearable electronics label with an output voltage of 355 mV. 2D GO films can be fabricated by vacuum filtering or via spontaneous evaporation from the solution. When one side of the GO film is insulated, while the other side is exposed to moisture, the asymmetric migration of water molecules into the film introduces an ionic current from the bare side to the insulated side of the active medium. This process also occurs in the porous structure of 3D GO foam, but the higher density of nanopores in this material facilitates the absorption and diffusion of water molecules resulting in higher power.
output. Freeze-drying, followed by heating or laser processing of MeA, gives a 3D GO foam containing a gradient in oxygenated functional groups and raises the output voltage to $\approx 1.5$ V.\(^{[45]}\)

### 4.1.2. Carbon Nanoparticles and Carbon Nanofibers

The high surface area and the abundance of functionalized adsorption sites on CNPs and CNFs make these materials promising candidates as active media in water-enabled electricity generators.\(^{[111]}\) When incorporated in a porous structure, the primary source of electrical power arises from streaming currents that lead to the establishment of a streaming potential. The interaction between individual CNPs and water molecules is determined by the surface properties of the CNP. The surface of a CNP can be either hydrophilic or hydrophobic depending on the nature and composition of the surface functional groups. It has been found that treatment in an oxygen plasma can make the surface more hydrophilic and increase surface energy, enhancing the reaction with water molecules.\(^{[16]}\) Due to the dissociation of the surface functional groups, the CNP surface is often negatively charged; releasing protons that can migrate along the nanochannel under the application of external pressure. For example, when liquid water enters a porous medium the capillary force can drive the migration of protons leading to the appearance of a streaming potential.\(^{[16,25,53]}\)

A WEEG based on the steady evaporation of water has been developed using carbon black as the active medium and generates a DC voltage of $\approx 1$ V when exposed to moisture in an ambient atmosphere.\(^{[16,25]}\) After annealing and plasma treatment, the CB film is composed of loosely stacked disordered graphene flakes with a specific area as high as 167 m\(^2\) g\(^{-1}\) and a high abundance of surface functional groups. The introduction of methylbenzene soot, ethylcellulose, terpineol, and ethanol into the CB, yields a robust composition that operates for more than 480 h producing a DC output voltage of up to 1 V.\(^{[25]}\) It is interesting that the output voltage of this device can be improved by increasing the ambient temperature and the wind speed, which act to decrease the ambient humidity in this kind of WEEG.\(^{[16,25]}\) By modifying the surface functional groups on the CNPs with polyethyleneimine (PEI), 1,2,3,4-butane tetracarboxylic acid (BTCA), and poly sodium-p-styrene sulfonate (PSS), the output voltage can be tuned to either polarity with outputs of $\approx 3$ V, $+$3 V, and $+$3 V, respectively.\(^{[53]}\) The maximum power densities are however quite low ($\lesssim 1 \mu\text{W cm}^{-2}$), but this can be increased to 0.243 mW cm\(^{-2}\) when polyaniline (PANI)/CNT and CaCl\(_2\) are used as the electrodes and water absorber, respectively.\(^{[83]}\)
4.1.3. Polymers

Many polymers containing hydrophilic functional groups are known to have excellent water absorption capacity due to the strong water affinity of active surface sites. As in polyelectrolytes, some polymers can release a high concentration of mobile ions and become electrically conductive when in contact with moisture. Polymers such as PSSA, PAAS, PVA composite, polyacrylic acid (PAA), hydroxyethyl cellulose, Naion, guar gum, and alginate sodium can be formulated into a membrane structure for applications in MEEGs.

A PSSA film with a dimension of 1 × 1 cm fabricated using direct casting can generate an open circuit voltage of 0.8 V in air at an RH of 80%. The enriched sulfonated functional groups release free protons when contacted with water molecules, which can then migrate along the moisture gradient and accumulate on one side resulting in a potential difference. The performance of this and similar devices can be tuned by changing the composition and structure of the active medium.

For example, a film combining PSS and PVA can be highly flexible, transparent, and self-healing, while maintaining a high capacity for the generation of electrical power in a WEEG. By combining PAA and GO, a continuous moist nanogenerator can harvest energy from moisture over a wide temperature range (−25 °C to +50 °C) and RH levels (5–95%).

4.1.4. Biomaterials

Biomaterials, including natural and synthesized materials, are attracting much attention as components in electronic devices as these materials are generally widely available, mechanically robust, biodegradable, and self-sustainable. Biomaterials now used in the assembly of WEEGs include cellulose nanofibers (NFs), biological nanofibrils, GO-PAAS: porous graphene oxide and PAAS composite, CB: carbon black, PPGO: an assembly of poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) and GO, Mg−CNF: direct contact between Mg alloy and CNFs, nGO-pGO: negatively and positively charged GO film, BCP-rGO: block copolymer-modified reduced GO.

Figure 7. A summary of materials used as the active medium in WEEGs together a comparison of output performance. a) Distribution of materials used in applications. b) Output voltage and power density for different materials. c) The output voltage and d) averaged voltage of single and integrated devices. The output here is either calculated or cited directly from the literature. (GO: graphene oxide, graphene oxide film, 3D graphene oxide membrane/foam, graphene quantum dots, GO fiber: graphene oxide fiber, CDs: carbon dots, CNT: carbon nanotubes, Bio NFs: biological nanofibrils, GO-PAAS: porous graphene oxide and PAAS composite, CB: carbon black, PPGO: an assembly of poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) and GO, Mg−CNF: direct contact between Mg alloy and CNFs, nGO-pGO: negatively and positively charged GO film, BCP-rGO: block copolymer-modified reduced GO.)

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The surface composition and high concentration of charge states in these materials make them effective in generating streaming currents but the streaming potential will vary with the type of material. Several experiments have shown that a combination of these materials with carbon black or GO can improve electrical output as ion gradient diffusion becomes the dominant mechanism for power generation.\textsuperscript{[69,85]}

A promising fabrication technique involving the direct printing of carbon dots on paper\textsuperscript{[85]} can produce a composite medium that produces electricity from water. In this device, the paper acts to absorb water giving the conditions that transfer protons originating from the dissociation of carboxyl groups. A WEEG constructed from a single sheet of printed paper was found to give an open circuit output voltage of 0.25 V and a short-circuit current of 15 nA.\textsuperscript{[101]} Unfortunately, while this is a simple and green way to harvest energy, the power density was found to be quite limited. Other biomaterials such as natural NFs extracted from softwood, crab shells, regenerated silk fibroin of Bombyx mori cocoons are demonstrated to have a higher energy conversion efficiency.\textsuperscript{[101]} Because of their intrinsic hydrophilicity, their ability to maintain streaming currents in the presence of evaporative flow, and the high density of surface charge these biomaterials can maintain a DC output over long periods of time. Chemically synthesized cellulose NFs combined with GO are also well suited as the active medium in high-performance WEEGs as this composite material has been found to facilitate the capture of moisture from humid air.\textsuperscript{[69]}

One innovation consists of the use of protein nanowire networks to build WEEGs based on the ionic gradient diffusion mechanism.\textsuperscript{[100]} In this case, a film containing the active medium was assembled from 3 nm diameter, 1–3 μm long nanowires, resulting in a network structure containing a random distribution of nanopores. This material is characterized by a low vapor for water inside the active medium enabling it to self-maintain a strong moisture gradient. These conditions are ideal for the long-term generation of electrical power (0.4–0.6 V for more than 2 months) using the WEEG configuration.

4.2. Solid Oxides

Metal oxides are viable alternatives for streaming current-based electricity generation as the surface of metal oxides is usually hydrophilic while the bulk material is relatively stable and does not disintegrate in the reaction with water molecules.\textsuperscript{[114]} While films consisting of TiO\textsubscript{2} nanostructures were the first metal oxide compositions developed for applications in WEEGs,\textsuperscript{[101]} silica has also been used as an active material for harvesting energy.\textsuperscript{[54,105]} An extensive-network structure with many interconnected nanochannels is obtained with these materials. The surface of these nanochannels develops a negative surface charge when exposed to moisture. Mobile cations in the EDL in a porous TiO\textsubscript{2} structure diffuse along with water molecules producing a streaming voltage of 0.5 V and a current density of 8 μA cm\textsuperscript{2} in a high humidity environment (RH ≈90%). The voltage output consists of sequential pulses since the moisture gradient in the sandwiched structure cannot be maintained at a stable state. In an evaporation-based WEEG using solid oxides such as Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, or ZnO, a DC voltage can be obtained by partially immersing the oxide film in deionized water.\textsuperscript{[104]} A 20 μm thick, 18 × 4 cm Al\textsubscript{2}O\textsubscript{3} film was found to generate an open output voltage of 2.5 V under standard atmospheric conditions. This output could be increased to 4.5 V by increasing the operating temperature and wind velocity. The short-circuit current was ≈0.8 μA while the maximum power obtained with an optimized resistive load was ≈0.51 μW. A WEEG device with a porous layer of Al\textsubscript{2}O\textsubscript{3} nanoparticles fabricated by vacuum filtration produced an open-circuit voltage of 4 V and an output power of 14.8 μW on exposure to a single 8 μL water droplet.\textsuperscript{[12]} Since the effective area for power generation is very limited due to the small volume of the water droplet, the output power density can be calculated to be ≈196 μW cm\textsuperscript{−2} (Figure 7b). This result indicates that WEEGs are capable of acting as sources with high power density. Another characteristic of the Al\textsubscript{2}O\textsubscript{3} nanogenerator is a rapid response time (3.4–15.8 ms) to changes in water content making them useful as water droplet sensors and water detectors.

4.3. Other Materials

In addition to the materials mentioned earlier, active media can be engineered to incorporate other materials such as Mg,\textsuperscript{[14,40]} Si,\textsuperscript{[68,107]} Ni–Al,\textsuperscript{[65]} Cu–Zn alloy,\textsuperscript{[108]} and glass fibers\textsuperscript{[53]} as an aid to increasing the overall electrical output. For example, a steady DC output voltage driven by natural evaporation of water can be obtained by painting Ni–Al on a layered double hydroxide (LDH) supported on a polyethylene terephthalate substrate.\textsuperscript{[65]} The output of this device is generated from streaming currents through the highly active charged nanochannels between Ni–Al LDH flakes.

Galvanic corrosion combined with the decomposition of water enables electricity generation from Mg-polyaniline when contacted with water droplets.\textsuperscript{[46]} It is remarkable that the power density can be as high as 0.2 mW cm\textsuperscript{−2} by the simple assembly of Mg and CNF.\textsuperscript{[114]} The oxidation of Mg at the anode releases Mg\textsuperscript{2+} and electrons, while H\textsubscript{2}O absorbed in the CNF cathode accepts electrons transported from the anode. Another redox-induced electricity generation device, using Cu–Zn as the active material and static droplets as the water source, has been reported for use in self-powered wearable electronics.\textsuperscript{[108]} It is found that superhydrophobic nanostructured surfaces present in this material are conductive and act to enhance output current and improve output stability. This type of WEEG produces an open-circuit output voltage pulse of ≈0.78 V and a power density of ≈30 mW cm\textsuperscript{−2} from a single 10 μL applied to the system.

5. Recent Advances in Improving Electrical Output

Due to an inherently low energy conversion efficiency, the output power delivered by a single WEEG is usually low (10\textsuperscript{−8}–10\textsuperscript{−3} W) and the highest output voltage is typically <5 V. Even though recent advances in the design and structure of these devices have resulted in significant improvements, the electrical power available from water/moisture-enabled generators is much less than that obtained from conventional power sources. This limitation represents a major challenge for some self-powered applications. For example, the power consumption of a Bluetooth system
ranges from several to tens of mW, which generally exceeds that available from most WEEGs. This situation can be improved by using supercapacitors to store the electrical energy produced moisture. This energy can then be accessed, as appropriate, by other electronic devices.

Fortunately, limitations on the voltage available from MEGs can be overcome by incorporating a number of units in a multiplexed configuration, so that output voltages of up to 1000 V can now be obtained. An example of such a multiplexed generator is shown in Figure 8. The construction of this MEG is based on the sequential offset stacking of individual asymmetric lipid bilayers of polyelectrolyte films (BPFs). These films contain a heterogeneous distribution of mobile Cl⁻ and H⁺ ions that can be released by reaction with water molecules on exposure to moist air. When Cl⁻ and H⁺ ions appear from the dissociation of the two layers in the bilayer structure, they move in opposite directions across the two layers establishing a voltage difference that can be read out with electrodes on either side of the structure. While this voltage difference is only 1.38 V, the layers can be offset and stacked sequentially as shown in Figure 8a. This stacking strategy, facilitated by laser machining of the electrodes, connects individual generators in series such that a total output voltage output of 1000 V can be obtained by joining 1500 units (Figure 8b). This heterogeneous moisture-enabled generator (HMEG) retains >80% of its electrical capacity after operating for 16 h. This electrical output can be used to charge a capacitor or lithium battery for subsequent applications in powering commercial electronics. In their report, Wang et al. show that the output of their HMEG is sufficient to power a 10 W lamp bulb (Figure 8b) or a dynamic electronic ink screen (Figure 8c). This technology then opens up many new possibilities for self-powered sensing, active communication, and data processing in IoTs. We can foresee a broad range of creative electronics and systems in health care, information, security, and environment applications deriving from this concept using sustainable power generation from MEGs.

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Figure 8. Assembly of an array consisting of stacked/offset bilayer polyelectrolyte films with interelectrode structures machined by laser cutting. This array acts as an MEG capable of producing an output voltage of 1000 V when exposed to air-borne moisture. a) Schematic illustration of the large-scale integration of individual MEG units connected in series and sequentially aligned using laser processing. b) Plot of the open-circuit voltage as a function of the number of individual MEG units. The inset shows a 10 W bulb powered by the output of this device. c) Demonstration of a self-powered electronic ink screen using the electricity from an MEG array. Reproduced with permission. Copyright 2021, The Nature Publishing Group.
6. Conclusions and Outlook

Alternative energy sources based on the harvesting of electrical power from the water present in terrestrial environments have now been identified as viable alternatives to conventional power generation technologies. Despite this promise, many challenges remain in the development of robust, high-output devices with sustained power generation capability. These challenges center on the optimization of surfaces to present structures and compositions that efficiently extract energy from water in liquid or in vapor form, and the engineering of these surfaces into compact self-contained devices. The first of these problems are being addressed by exploiting recent advances in nanotechnology and materials synthesis to the extent that a creative approach in tailoring surfaces has led to vast improvements in power generation from generators based on liquid water (WEEGs) and moisture (MEGs). Engineering has also greatly enhanced the capabilities of both types of generators, as indicated by the multiplexing of many individual MEGs to obtain voltage outputs of up to 1 kV.[11] Power output has also been improved significantly with recent reports of ≈0.2 mW cm⁻² from a simple device based on Al₂O₃ nanoparticles.[12] These studies indicate that further improvements in the performance of WEEG and MEG devices will focus on the optimization of active materials for the extraction of energy in compact robust systems. The primary areas of interest are: 1) finding compositions that are highly porous so that water molecules and ions can easily diffuse/migrate in the active medium; 2) synthesizing materials that are electrically insulating but that have high ionic conductivity facilitated by charge hoping; 3) hydrophilic materials with a low activation energy for reaction with water; 4) methods of increasing the surface density of active functional groups so that an abundance of ions are released when the surface is contacted by water molecules; 5) active media that consist of a rigid framework with high mechanical strength so that they are unaffected by repetitive exposure to water and mechanical loading; and 6) finding ways to allow these materials to generate a constant DC power output or a predictable, reproducible series of electrical pulses for an extended period of time. In addition, WEEGs and MEGs must incorporate low-cost, sustainable, and environmentally friendly materials, and be inexpensive to manufacture to encourage future commercialization opportunities.

As we have shown in this review, many materials have been found to satisfy a number of these criteria, and can generate electricity from water and/or moisture, but most of these materials do not combine all of the ideal characteristics listed above. For example, metal-oxide-based devices can generate high output voltages and are mechanically robust but tend to disintegrate when in contact with water for an extended time, while graphene-based devices can be highly flexible but are expensive. Apart from these materials-related aspects, there is a great need for the development of structures that enhance the interaction of water with the active medium while minimizing the overall profile of the device under operating conditions. Integration of these generators with electrical energy storage devices such as batteries or supercapacitors is also important if the output power is intermittent or insufficient to drive electronics in a specific application. An important consideration in this regard is the design of new efficient assembly techniques that enable the interconnection of multiple devices to improve electrical output while minimizing the volume of the assembled package. This requirement is especially important if WEEG and MEG units are to be adopted as stand-alone power sources in health care, security, information, and artificial intelligence applications.

The enticing concept of green energy obtained in a sustainable way from readily available, non-polluting, resources is now the driving factor for this rapidly developing field, but the commercialization of this technology will require a collaborative effort across many fields of science and engineering. In this context, the development and application of WEEGs and MEGs offer a unique opportunity for collaborative research with the goal of mitigating some aspects of the energy crisis while maintaining environmental integrity.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] S. Chu, Y. Cui, N. Liu, Nat. Mater. 2017, 16, 16.
[2] K. W. J. Barnham, M. Mazzer, B. Clive, Nat. Mater. 2006, 5, 161.
[3] M. Höök, X. Tang, Energy Policy 2013, 52, 797.
[4] R. York, Nat. Clim. Change 2012, 2, 441.
[5] C. McClade, P. Ekins, Nature 2015, 517, 187.
[6] H. Lund, Energy 2007, 32, 912.
[7] F. R. Fan, Z. Q. Tian, Z. L. Wang, Nano Energy 2012, 1, 328.
[8] S. Roundy, P. K. Wright, Smart Mater. Struct. 2004, 13, 1131.
[9] W. He, G. Zhang, X. Zhang, J. Ji, G. Li, X. Zhao, Appl. Energy 2015, 143, 1.
[10] D. Shen, M. Xiao, G. Zou, L. Liu, W. W. Duley, Y. N. Zhou, Adv. Mater. 2018, 30, 1705925.
[11] D. Shen, W. W. Duley, P. Peng, M. Xiao, J. Feng, L. Liu, G. Zou, Y. N. Zhou, Adv. Mater. 2020, 32, 2003722.
[12] X. Zhao, J. Feng, M. Xiao, D. Shen, C. Tan, X. Song, J. Feng, W. W. Duley, Y. N. Zhou, ACS Appl. Mater. Interfaces 2021, 13, 27169.
[13] Z. Hui, M. Xiao, D. Shen, J. Feng, P. Peng, Y. Liu, W. D. Duley, Y. N. Zhou, Nano-Micro Lett. 2020, 12, 5.
[14] J. Feng, M. Xiao, Z. Hui, D. Shen, Y. Tian, C. Hang, W. W. Duley, N. Y. Zhou, ACS Appl. Mater. Interfaces 2020, 12, 24289.
[15] F. Zhao, H. Cheng, Z. Zhang, L. Jiang, L. Qu, Adv. Mater. 2015, 27, 4351.
[16] G. Xue, Y. Xu, T. Ding, J. Li, J. Yin, W. Fei, Y. Cao, J. Yu, L. Yuan, L. Gong, C. Shen, S. Deng, J. Zhou, W. Guo, Nat. Nanotechnol. 2017, 12, 317.
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