All-Weather-Compatible Hydrovoltaic Cells Based on Al$_2$O$_3$ TLC Plates

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ABSTRACT: Electrical power can be extracted from interactions at the interface of water/materials, known as the “hydrovoltaic” phenomenon. Devices based on this emerging technology hold a lot of promise for meeting renewable energy demands, but materials reported to date largely require specific weather conditions, such as low humidity (~10–30%), thus hindering widespread application. Herein, we report a new use of plates for thin layer chromatography (TLC) that provide a continuous support of capillary-driven water flow. When coated with α-Al$_2$O$_3$, this simple 8 cm$^2$ device can produce a continuous voltage of ~0.33 V and a short circuit current of ~0.85 μA over a wide range of humidity (10–90%). Low cost, stability against surface reactions, ease of fabrication, and power output under varied weather conditions make this device a realistic possibility for use in renewable power generation applications.

INTRODUCTION

Hydrovoltaic devices are an emerging technology that can extract power at the interface of porous materials in contact with water, whether the water is in the form of humidity, flowing water, from rainfall, wetting a surface through capillary action, followed by evaporation, and more.1,2 Most studies have focused on maximizing the power output (maximizing open circuit voltage—$V_{oc}$ and/or short circuit currents—$J_{sc}$) using cost-effective carbon substrates. For example, in the pioneering work of Guo et al., 2.5 cm$^2$ soot substrates from burning fuels have been used to achieve 1 V under open circuit conditions; one of the highest efficiency hydrovoltaic devices to date.3 As such, hydrovoltaics is becoming a burgeoning area of interest to produce power at low cost and with renewable materials, thus reducing the impacts of power generation on global warming and environmental pollution.4–10 Recent advances have shown an impressive $V_{oc}$ of 2.5 V with 72 cm$^2$ metal oxide-based films,11 or a $J_{sc}$ of over 55 mA cm$^{-2}$ with silicon nanofiber-based nanogenerators,12 both requiring a specific environment of 10–30% humidity and a temperature of 25–40 °C.

Water evaporation (Figure 1) has been highlighted as the most promising method for power generation because these devices function in most of the environments.11–15 Some of the challenges faced by these devices are their complex synthesis, reproducibility, weak adhesion with substrates, and poor mechanical flexibility, which have been addressed with: (i) polymer modifications for an extra support, (ii) deposition of thick films of nanomaterials to increase their adhesion power with substrates, and (iii) plasma and/or chemical treatment to increase hydrophilicity.15–19 However, constructing an all-weather condition functional hydrovoltaic device has remained elusive; these devices become inactive when atmospheric conditions reach 100% relative humidity (RH).3,9–11

In this report, an “all-weather” functional hydrovoltaic device constructed by depositing α-Al$_2$O$_3$ (size approx. 200 nm) on a thin layer chromatography (TLC) plate substrate is investigated. The design is both simple and has favorable attributes, including: (1) a high rate of capillary flow due to high porosity and (2) stability against degradation under working conditions. At neutral pH, α-Al$_2$O$_3$ has a positively charged surface (a zeta potential of +40.3 mV),16–18 and firmly adsorbs onto the alumina surface without the use of any additional adhesives. Therefore, α-Al$_2$O$_3$ adsorbed on porous Al$_2$O$_3$ substrates is an ideal choice for simple electrokinetic devices.

EXPERIMENTAL SECTION

Materials and Methods. Aluminum oxide powder ($α$ phase), with an average particle size of 20–50 μm and a purity of 99.9%, was obtained from Alfa Aesar and used without further purification. Sigma-Aldrich provided neutral aluminum oxide TLC plates with a $L \times W$ of 20 × 20 cm. Ethanol (95% from Commercial Alcohol Inc.) was used as a solvent. Copper paper electrodes were purchased from Dongguan Kaidi...
Adhesive Technology Co Ltd. and graphite electrodes were purchased from American Elements Inc. MilliQ water was used for all hydrovoltaic measurements.

**Hydrovoltaic Device Fabrication.** A typical device fabrication process is illustrated in Figures 2 and S1. Briefly, a TLC plate (20 × 20 cm) was calcined at 80 °C for 12 h to remove any moisture. Next, a suspension of α-Al2O3 (0.5 gm/mL) in ethanol was uniformly spread on the TLC substrate and allowed to air-dry for several minutes and subsequently was further dried for 12 h at 80 °C to ensure proper adhesion of the alumina layer on the TLC plate to prevent from leaching into water and provide maximum stability. The thickness of Al2O3 and α-Al2O3 was ∼18 and ∼10 μm, respectively (measured with a micrometer). The substrate was cut into 4 × 6 cm, and excess alumina was removed with a blade to a final size of 2 × 4 cm and cleaned with ethanol. Copper tape was used as an electrode support, pasted at the bottom and top of α-Al2O3-coated TLC plates, acting as counter and working electrodes.

**Hydrovoltaic Measurements.** All hydrovoltaic measurements were carried out using a Metrohm potentiostat. Copper tape was used as a counter and working electrode, and MilliQ water was used as a solvent. First, the open circuit voltage was measured to determine the open circuit potential (OCP) from various devices. Furthermore, linear sweep voltammetry (LSV) was then used to measure the short circuit current (Isc), and cyclic voltammetry was used to study the non-faradic behavior of the electrodes. Furthermore, OCP and LSV were measured at different load resistances to estimate the maximum power output of the device.

**RESULTS AND DISCUSSION**

The hydrovoltaic performances of an α-Al2O3-coated TLC plate and a TLC plate are compared in Figure 3. Both Voc and Isc are drastically increased with the deposition of a top α-Al2O3 layer.

Device performance metrics are summarized in Table 1 and are determined after an ~1000 s equilibration time (see Figure 3). Importantly, the α-Al2O3 device exhibits continuous potential indefinitely (recorded for >18 h, Figure S2) with five devices measured to ensure accuracy of hydrovoltaic metrics. To test the device’s stability, OCP was recorded over 7 days with >300 mV retained throughout, Figure 4a. Importantly, repeated LSV measurements show consistent voltages and currents, indicating no measurable changes to structural integrity or surface reactivity of these devices, Figure 3a. Furthermore, to confirm that the power generation is solely due to capillary and evaporation phenomena rather than chemical reactions of copper electrodes, Voc was measured using an inert (graphite) electrode, which produced a similar voltage to those of copper electrodes, Figure S3.

To further evaluate the all-weather compatibility and to determine the optimal conditions for the device, performance was evaluated in a humidity-controlled chamber. The RH of the chamber was controlled between 10 and 90% and Voc values were measured (Figure 4b). Humidity has little effect on Voc from 10 to 90% RH. Beyond 90% RH (sealed system), capillary action ceases and Voc drops dramatically, Figure S4. Surprisingly, there is also little effect on the current upon increasing humidity from 10 to 90% beyond which the hydrovoltaic effect is limited only under sealed conditions. This demonstrates that providing a porous support, such as a TLC plate in this case, assists in sustaining the water flow even
at higher humidity, carrying charges through the main substrate and generating a streaming potential.

To further explore the “all-weather condition” capabilities, variables such as the arrangement of electrodes and the salinity and pH of water sources were explored. It was found that the electrode arrangement used (see Figure 1) was necessary for observing the hydrovoltaic phenomenon; consistent with a streaming potential being the major mechanism of charge generation. A series of experiments were carried out to explore the electrode arrangement effect on HV performance for devices prepared from $\alpha$-Al$_2$O$_3$-coated TLC plates, shown in Figure S5. When a glass plate with two electrodes was partially submerged in water or is measured with no water, there was no measurable output potential or current, indicating that both $\alpha$-Al$_2$O$_3$ and water are necessary for electricity generation. Also, when the copper electrodes were pasted parallel to the flow direction of water, that is, vertically, the device showed a negligible power output. A potential difference was only observed between the bottom and top of the device when placed half-submerged in water, supporting an electrokinetic phenomenon, where electric double layer formation occurs at the heterogeneous interface between the solid surface and water. The EDL formation arises from solvation of water molecules under the electric field of the polarized solid surface. Anions are attracted, while the cations are repelled, resulting in distribution of charges near the solid surface and formation of

| Hydrovoltaic Device | $I_{sc}$ (nA) | $V_{oc}$ (mV) |
|---------------------|--------------|--------------|
| TLC plate           | 25           | ~50          |
| RH = 10%            |              |              |
| $\alpha$-Al$_2$O$_3$-coated TLC plate | 850          | 330          |
| RH = 10%            |              |              |
| TLC plate           | 10           | 40           |
| RH = 100% (sealed)  |              |              |
| $\alpha$-Al$_2$O$_3$-coated TLC plate | 150          | 88           |
| RH = 100% (sealed)  |              |              |

“Note: all measurements were performed at 20 °C with variations of ± 2 °C.

Figure 3. (a) LSV measurement of TLC (red line) and $\alpha$-Al$_2$O$_3$/TLC (black line), performed 10 times to illustrate the stability and reproducibility of this measurement and (b) OCP measurement of an alumina (TLC) plate (red line) and an $\alpha$-Al$_2$O$_3$-coated TLC (black line) at 10% RH and 20 °C.

Figure 4. (a) Measured OCP values of $\alpha$-Al$_2$O$_3$/TLC for 7 consecutive days and (b) OCP and short-circuit current values as a function of humidity (obtained from LSV measurements under each humidity as indicated).

Figure 5. $V_{oc}$ and $I_{sc}$ generated from the different water and salt concentrations under ambient laboratory conditions (20 °C and RH = 40%).
In our test system, an EDL layer is formed due to interaction of water molecules with a positively charged coated layer of α-Al₂O₃ nanoparticles (Figure 1). The repelled positive ions concentrate in water, while hydroxyl anions move with the water and are collected at the top electrode. From this movement of charges, a streaming potential (voltage) is generated. We denote the $V_{oc}$ sign of this direction as positive, as shown in Figure 1.

To explore the ionic strength effect on HV performance, the device performance was measured at different ionic concentrations. As shown in Figure 5, $V_{oc}$ is inversely dependent on the NaCl concentration in a range of $10^{-2}$ to $10^{-1}$ M. This concentration dependency is a further confirmation of a streaming potential driven by the electrokinetic effect. However, a drop in both $V_{oc}$ and $I_{sc}$ was observed beyond an electrode separation of 4 cm due to competing effects of a thinner width of a capillary water versus faster evaporation leading to deprivation of anions reaching the top electrode. Keeping the height fixed at 4 cm, a longer device with a width of 15 cm was fabricated that showed an $I_{sc}$ up to $\sim 2.4 \mu$A.

To assess the device under real working conditions, an 8 cm² α-Al₂O₃ substrate was connected to different load resistances ($R_L$). Figure 6a shows the output voltage and current dependence on load resistance. With load resistance between 1 Ω and 10 kΩ, the voltage was negligible (0.00 to 0.008 V); however, when the load resistance was further increased from 10 kΩ to 22 MΩ, the voltage increases to 0.290 V. A maximum output power of 40 nW, equivalent to a power density of 5 μW/cm³, is achieved with an $R_L$ of 100 kΩ (Figure 6b).

The power output can be simply amplified by either series or parallel combinations of different devices. In this experiment, 12 devices prepared from α-Al₂O₃ were connected in a series fashion, which increased the voltage output to 3.8 V, expected from the addition of individual voltages, Figure 7a. An application demonstration of the α-Al₂O₃ substrate as a practical power source for energy storage is shown in Figure 7b. Three series connected α-Al₂O₃ devices can charge a 100 μF capacitor to 0.86 V in 2000 s.

This increase is possibly due to the faster evaporation rate when the water travels to a higher capillary height, resulting in a higher accumulation of charge carriers. However, a drop in both $V_{oc}$ and $I_{sc}$ was observed beyond an electrode separation of 4 cm due to competing effects of a thinner width of a capillary water versus faster evaporation leading to deprivation of anions reaching the top electrode. Keeping the height fixed at 4 cm, a longer device with a width of 15 cm was fabricated that showed an $I_{sc}$ up to $\sim 2.4 \mu$A.
on favorable conditions for power generation, such as a high wind speed and a high temperature, but did not provide detailed results at different humidity levels.\textsuperscript{29,30} However, herein, we demonstrate power generation under extreme humidity conditions, which can provide guidance for next-generation hydrovoltaic devices.

**CONCLUSIONS**

Using a simple \( \alpha-Al_2O_3 \)-coated TLC plate template, we have fabricated hydrovoltaic devices that are able to perform under a wider range of humidity (10–90% RH) and temperature (0–45 °C) conditions. A standardized \( \alpha-Al_2O_3 \) substrate with an effective size of 8 cm\(^2\) produced a continuous \( V_{oc} \) of \( \sim \)0.33 V and an \( I_{sc} \) of \( \sim \)850 nA over a wide range of humidity (10–90% RH). A single \( \alpha-Al_2O_3 \) device was able to produce a maximum power density of 5 \( \mu W/cm^3 \) under a load of 100 k\( \Omega \). The ability to generate power under \( \sim \)90% RH and sustaining activity for an indefinite time are remarkable features, which combined with a low cost, simple scale-up, easy fabrication, and a near universal design make this substrate viable for energy production.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04751.

Additional hydrovoltaic performance measurement data; fabrication procedure of hydrovoltaic devices; and assessment of all-weather performance and reproducibility of the fabricated devices (PDF)

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Funding
The research presented herein was supported by the New Frontiers in Research Fund (NFRF) program, Natural Science and Engineering Research Council (NSERC) through the Discovery Grant program Award Number RGPIN-2016-05070, and the Canadian Foundation for Innovation under the John R. Evans Leaders Fund program.

Notes
The authors declare no competing financial interest.

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