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Empowering Zero-Energy Buildings with Cutting-Edge Self-Powered Electrochromic Smart Window Technology

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The development of energy-efficient window technology is crucial for zero-energy building approaches, as windows play a pivotal role in minimizing heat loss, optimizing natural light utilization, and contributing to overall energy conservation. In this study, a self-powered electrochromic smart window is presented together and its application as a self-charging battery is showcased. The self-powered system is composed of a WO_x electrochromic working electrode, an Al counter electrode, and an $AlCl_3$ liquid electrolyte similar to a voltaic cell. This device generates an open circuit voltage of around 0.95 V. When two electrodes are connected, this voltage is applied as an external voltage and changes the color of the transparent WO_x electrode into a blue state with approximately 62% transmittance modulation. However, if the two electrodes are connected via an light-emitting diode (LED), the LED lights up for up to 4 h.

1. Introduction

Electrochromism is the reversible modulation of a material's color and optical characteristics through a chemical reduction/oxidation process.[1–3] Electrochromic devices (ECDs) enhance occupant comfort by mitigating glare and optimizing daylight, increase privacy through on-demand tinting, and have extended lifespans due to the absence of moving parts commonly found in traditional shading systems.[4] Due to these benefits, ECDs have gained significant interest as windows capable of minimizing building energy consumption by dynamically regulating light and heat transmission.[5] Though ECDs operate at low voltages (<3 V), their external energy demand makes conventional electrochromic smart windows unsuitable for zero-energy building applications.[6]

The development of a self-powered electrochromic window (SP-EW) addresses this challenge without relying on external power supplies. Although some so-called self-powered devices driven by motion, solar cells, rechargeable batteries, nanogenerators, etc. have been reported, these devices often face limitations in practical applications in terms of scalability, efficiency, reliability, and low power output.[7–10] That's why in recent years totally self-powered windows driven by internal electrochemical potential gradients have gained considerable interest.[11,12]

An electrochemical cell comprises an anode, cathode, and electrolyte, facilitating the generation of electric current through spontaneous oxidation-reduction reactions.[13] The fundamental characteristics of anode and cathode materials lie in their ability to store and release ions. Electrochromic materials, renowned for their capacity to store and release ions and electrons during switching processes, demonstrate the battery electrode property.[14] The potential difference between the anode and cathode creates the voltage of the cell, serving as the driving force for the flow of electrons through the external circuit. This paradigm shift represents a novel approach to harness energy for sustainable applications by using the energy difference between the working electrode and counter electrode of EC devices in a suitable electrolyte. In some cases, this integration not only facilitates energy harvesting for this device itself but also other electronic devices to enhance energy efficiency in buildings.[15]

However, the limitations of current self-powered devices are multifaceted. Wang et al. (2013) reported self-powered device shows 52.2% color modulation but more than 4 h of recovery time.[12] Later Wang et al. (2021) proposed a device that shows improved recovery time (less than 700 s) but low coloration modulation (40%).[16] In contrast, Ma et al. (2023) reported device demonstrates both high modulation (>70%) and fast recovery time (<5 s) but needs two counter electrodes which makes the device operation complex.[11]

In this study, we focused on developing a simple operation, high-performance, low-cost, and sustainable, totally self-powered electrochromic window technology using WO_x electrochromic electrode. Due to the corrosion resistivity, high conductivity, cost-effectiveness, and lightweight characteristics, the Al electrode was used as the counter electrode.[17] Further, the $AlCl_3$ electrolyte was chosen over other electrolytes (NaCl, KCl, etc) because of its compatibility, support for desired redox reactions

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involving aluminium ions, the solubility of aluminium species, and ability to provide sufficient conductivity.

2. Results and Discussion

The ability of electrochromic devices to undergo reversible optical changes through ion and electron transfer renders them highly attractive for enhancing energy efficiency in buildings. WO_x, a widely recognized electrochromic material capable of undergoing reversible color changes, was investigated as a battery electrode material. In a 0.5 M $AlCl_3$ electrolyte, the potential difference between the WO_x cathode and anode materials like Cu, Al, and Mg was measured. **Figure 1**a shows that the potential difference between the WO_x electrode and Cu, Al, and Mg electrode is 0.36, 0.95, and 1.94 V respectively. If we connect two electrodes this voltage acts as an external voltage in the closed state and the color of the transparent WO_x window changes to blue. According to the value of the potential difference extracted by different electrodes, the colored state's transmittance is reduced by different extents (Figure 1b). Though the Mg electrode exhibits somewhat better performance than the Al electrode, due to its corrosive and less stable characteristics, the Mg electrode is not a good choice for a sustainable self-powered window design. In 0.5 M $AlCl_3$ electrolyte, the bleached state and the colored state of the WO_3 window in combination with the Al electrode are shown in Figure 1c,d.

To optimize the $AlCl_3$ electrolyte concentration, we prepared the different concentrations of electrolytes (e.g., 0.1 M, 0.5 M, etc.) and measured respective the transmittance change (**Figure 2**a). As the molarity increases, there is a slight decrease in the transmittance of the colored state, which increases the maximum transmittance modulation of the device. However, the higher concentrations of $AlCl_3$ electrolyte degrade the WO_x electrode materials over time. That's why to maintain stable and durable performance, we selected 0.5 M $AlCl_3$ as the optimized concentration in this device.

This electrochromic device exhibits robust performance not only in aqueous electrolytes containing $AlCl_3$ but also in other ionic electrolytes like NaCl and KCl. However, the device shows maximum transmittance modulation in the presentence of $AlCl_3$ electrolyte compared to NaCl and KCl (Figure 2b), due to the higher ionic conductivity of $AlCl_3$ (Figure 2c).

Figure 3a indicates that the device shows fast coloration and high transmittance modulation, by decreasing the transmittance curve sharply from 93% to 6% in 25 s. But the spontaneous bleaching process of this device is relatively slow, due to the absence of any external effect. In the coloration process, whenever we connect two electrodes, the Al electrode gets oxidized (Equation 1), and the WO_x electrode gets reduced (Equation 2), thereby transparent WO_3 electrode changes into blue.

$$Al = Al^{3+} + 3e^- \quad (1)$$

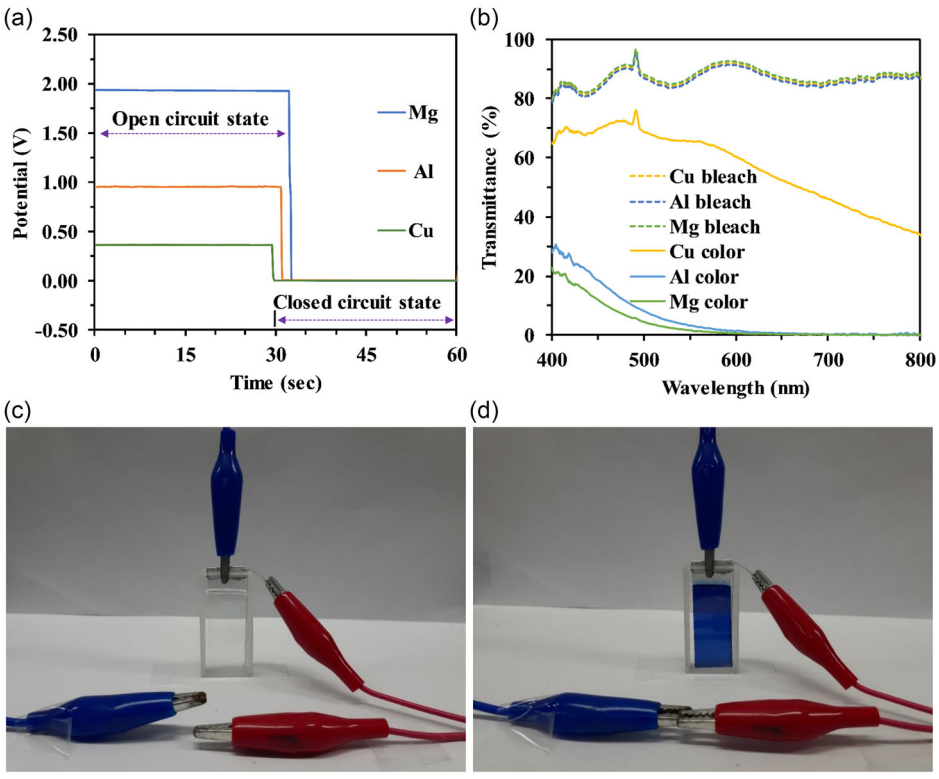

Figure 1. a) Battery characteristics of WO_x electrochromic electrode producing voltage in an open circuit state in combination with Cu, Al, or Mg electrode; b) WO_x self-powered electrochromic window bleached and colored states transmittance, utilizing the open circuit voltages in the closed states; and c) transparent and d) opaque state of WO_x self-powered smart window in a 0.5 M $AlCl_3$ electrolyte.

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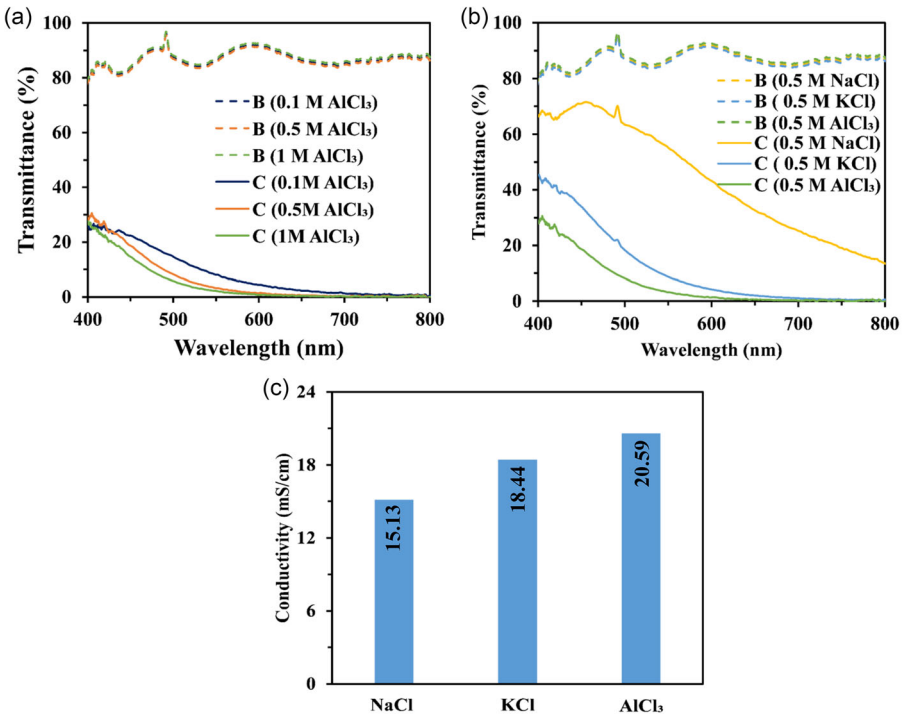

Figure 2. a) Effect of $AlCl_3$ electrolyte concentration, with increasing molarity, the coloured state transmittance decreases slightly; b) the operation of this Al/WO_x self-powered device with versatile ionic electrolytes (NaCl, KCl, etc.) (in Figure 2a,b, B and C represent bleached and colored states respectively); and c) comparison of ionic conductivity of 0.20 M NaCl, KCl and $AlCl_3$ aqueous electrolytes at 21 degrees Celsius temperature.

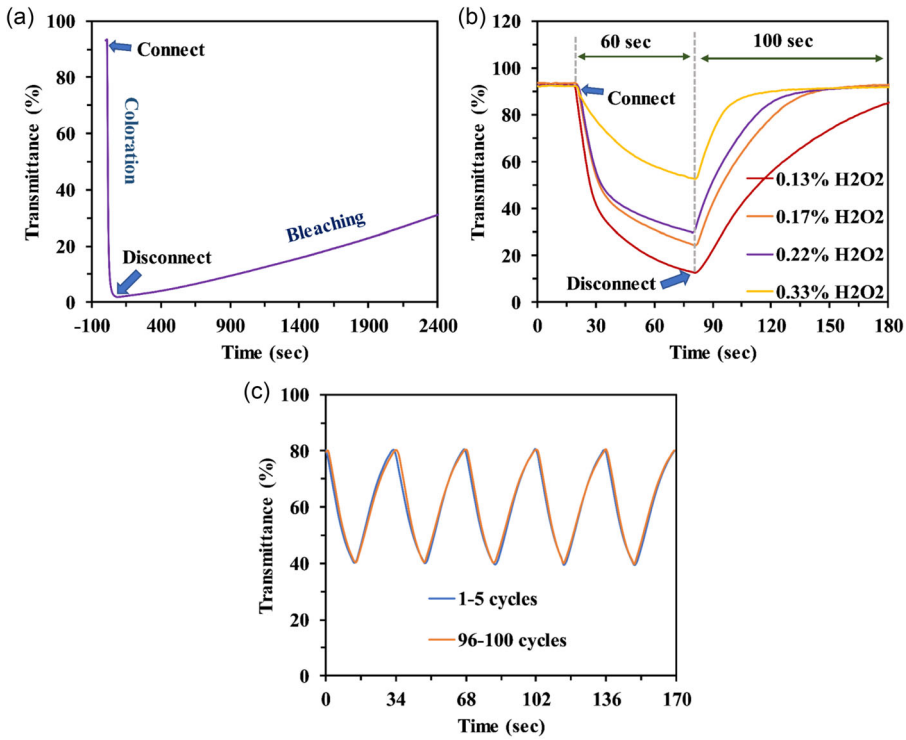

Figure 3. a) The in-situ transmittance change measurement of the WO_x EC device in the coloration and bleaching process, connecting and disconnecting with the Al electrode at 600 nm wavelength; b) decrease of the spontaneous bleaching time by adding different concentration of H_2O_2 in 0.5 M $AlCl_3$ electrolyte; and c) repeated coloration and bleaching process tested for 100 cycles using 0.5 M $AlCl_3$ + 0.22% H_2O_2 electrolyte, shows almost stable characteristics over time.

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Table 1. The effect of H_2O_2 concentration with 0.5 M $AlCl_3$ electrolyte on maximum transmittance modulation, coloration, and bleaching time to optimize the self-powered device's overall performance.

H_2O_2 concentration [%]	Max. trans. Modulation [%]	Coloration time [s]	Bleaching time [s]
0.13	80[a)]	37[a)]	90[b)]
0.17	68[a)]	40[a)]	49[a)]
0.22	62[a)]	38[a)]	44[a)]
0.33	40[b)]	46[b)]	38[a)]

[a)]A higher number of asterisks; [b)]Indicates better performance.

$$WO_x + y Al^{3+} + 3ye^- = Al_yWO_x \quad (2)$$

In contrast, in the bleaching process, when we disconnect two electrodes, the Al_yWO_x reacts with O_2 and changes to transparent WO_x spontaneously (Equation (3)).

$$4Al_yWO_x + 12\,H^+ + 3O_2 = 4WO_x + 4yAl^{3+} + 6H_2O \quad (3)$$

Later, to increase the O_2 molecule in the electrolyte and make the device suitable to work in a sealed state also properly, we added H_2O_2 (30%) into 0.5 M $AlCl_3$ electrolyte (Figure 3b). Though H_2O_2 decreases the bleaching time, its concentration should be optimized strictly, otherwise, excess concentration

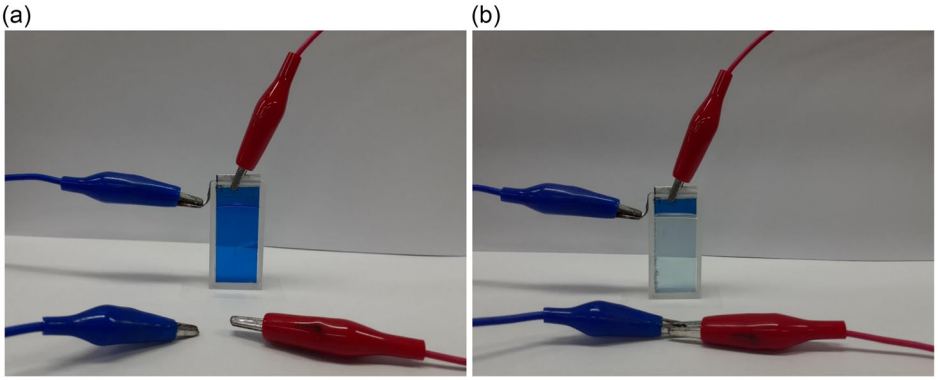

Figure 4. a) Colored and b) bleached state of Prussian blue (PB) self-powered smart window assembled with Al electrode in a 0.5 M $AlCl_3$ electrolyte.

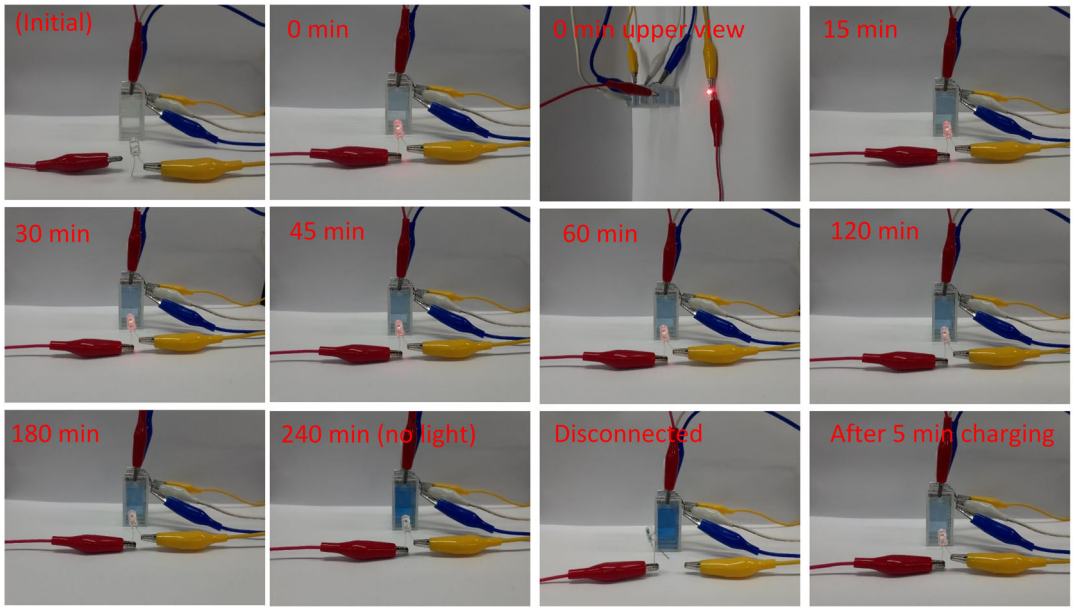

Figure 5. Photos of the as-prepared Al/ WO_x device, three cells connected in series acting as a self-rechargeable battery. The images were taken before connecting the LED; after connecting at 0, 15, 30, 45, 60, 120, 180, and 240 min; when disconnected for self-charging; and after 5 min charging in radiant state.

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of O_2 molecule significantly increses the coloration time also, and thereby the maximum color modulation (Figure 3b).

Table 1 shows that a low concentration of H_2O_2 results in high color modulation and fast coloration time, but it is associated with a slower bleaching time. After experimenting with various concentrations of H_2O_2, ranging from 0.13% to 0.33%, we successfully fine-tuned and identified the optimal concentration at 0.22%, where the maximum transmittance modulation is 62%, coloration time is 38 s and bleaching time is 44 s (for 90% transmittance change of maximum modulation) which surpasses the previously reported self-powered EC device performance.[12,18,19]

The repeated coloration and bleaching ability of this device was tested for 100 cycles (Figure 3c). The overlap graphs of the first 5 (1–5) and last 5 (96–100) cycles indicate that the device shows not only reversible but also stable characteristics over time. Further, it was examined that using our established system, Al counter electrode and $AlCl_3$ + H_2O_2 electrolyte, some other electrochromic electrode also changes color and work as self-powered smart windows such as Prussian blue (PB) as shown in **Figure 4**.

This self-powered smart window can also be used as a self-rechargeable battery which makes this window perfect as a design component in zero-energy buildings. **Figure 5** vividly illustrates the application of our smart window as a self-rechargeable battery, illuminating a small white light-emitting diode (LED) light. The captivating sequence captures moments at 0, 15, 30, 45 min, and beyond. Remarkably, the light remains consistently bright for up to 2 h, showcasing the reliable and sustained power output of our device. Beyond this duration, a gradual dimming of the light occurs, reaching a point of no illumination after 4 h. Concurrently, the device undergoes a fascinating transformation from its initial transparent state to a distinctive blue hue, signalling a discharged state. However, following disconnection, the device initiates a self-charging process, emitting a luminous glow within a 5-min interval. This dynamic interplay of light and color not only emphasizes our device as a self-rechargeable battery but also hints at the potential for sustained, eco-friendly energy solutions in diverse applications. The graphical interpretation of this device and its working principle is shown in **Figure 6**.

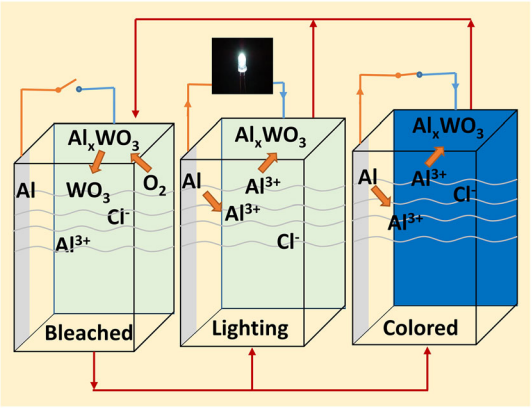

Figure 6. The graphical representation of the device structure and it's working principle either as a self-powered electrochromic smart window or self-rechargeable battery.

3. Conclusion

In summary, this report demonstrates a highly efficient, optimized design self-powered EC smart window for zero-energy buildings. Blocking heat transfer and sunlight improves energy efficiency and resident comfort in buildings. In 0.5 M $AlCl_3$ + 0.22% H_2O_2 electrolyte, this Al/WO_x device works as a voltaic cell and generates a voltage for itself. Using this voltage, the transparent WO_x electrode goes into a blue color state and by disconnection recovers its voltage within 33 s, thereby preparing for repeated coloration. This system also suitable for PB electrodes confirms their versatility. Further, as a battery, it can power up other electronic devices (e.g., LED light) which addresses the energy solution in an eco-friendly way and works as a complementary source for solar, wind, or other non-conventional resources to a small extent.

4. Experimental Section

Synthesis of WO_x Film: Substrate Preparation: An ITO PET film with properties, a resistance of 30 Ω cm^{-2}, a width measuring 0.6 m, and a length extending to 200 meters was used as the substrate. This flexible substrate underwent a meticulous plasma modification to fortify the adhesion properties of the substrate.

Large-Scale WO_x Electrode Fabrication: We employed large-scale fabrication of the WO_x electrode using a roll-to-roll (R2R) slot-die wet coating (Narae Nanotech Co., Ltd., S. Korea, slot die wet coater) technique. Light green WO_x ink precursor solution, with a solid content of 15.9% and a viscosity of 15 cp, having undergone 30 min of constant stirring, served as the liquid precursor for WO_x. Following a 2-min thermal treatment at 130 °C, the resultant WO_x ($x \approx 2.23$, Figure S1, S2, Table S1, Supporting Information) layer exhibited a thickness of roughly 550 nm (Figure S3, Supporting Information).

Preparation of Aluminum Electrode: A flexible aluminium sheet boasting a thickness of 0.4 mm and dimensions of 45 × 2 mm was harnessed as the counter electrode for our ECD.

Fabrication of ECD: For the full device fabrication, the WO_3 working electrode was carefully cut into dimensions of 40 millimeters by 15 millimeters. Then the WO_x working electrode and Al counter electrode were attached with glass slides to make the device robust. Using common glass slides of 40 ×6 mm, a compact device of dimensions 20 × 10 × 40 mm was fabricated.

Characterization Approaches: The measurement of optical characteristics was conducted employing a spectrometer (USB2000+) coupled with a UV-VIS-NIR light source (DH-2000-BAL), both sourced from Ocean Optics, Inc., USA. Evaluation of electrical properties was carried out using an electrochemical workstation (CHI1030 Multi-potentiostat), manufactured by CH Instrument, Inc., USA. To determine ionic conductivity, measurements were performed utilizing the (Orion Star A212) conductivity benchtop meter provided by Thermo Scientific.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

M.H.H.: Conceptualization, methodology, data curation, and draft writing. C.S.A.: Methodology, data curation, investigation, and validation. H.R.: Investigation, project administration, review, and editing.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

electrochromic windows, self-powered devices, self-rechargeable batteries, zero-energy buildings

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