

IN-SOIL BIODEGRADABLE ZN-AIR BATTERIES

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ABSTRACT

Increasing interest in data collection for agricultural and environmental sciences has created a need for long-term soil monitoring by wireless sensors. However, implementation of such sub-surface sensors may require on-board power, both for sensor functionality as well as wireless communication. To address this issue, we present Zn-air batteries built from biodegradable materials that can operate on or under the soil. Wax-encapsulated Zn-air electrochemical cells ('batteries') were fabricated based on thin film anodes, catalyst-bearing paper cathodes, and biodegradable gel electrolyte. The batteries provided a stable output voltage of over 1.2 V in soil for a week under relevant sensor discharge conditions.

KEYWORDS

Zinc-air batteries, biodegradable, long-term, in-soil condition

INTRODUCTION

Recent advances in sensor fabrication, wireless communication, and data analysis have led to the establishment and widespread implementation of wireless sensor networks (WSNs). Such networks can be a powerful tool for monitoring large physical areas in a variety of applications, including the natural environment as well as agriculture [1]. The deployment of a variety of subsurface sensors that monitor ambient conditions such as soil moisture, temperature and nutrient level, enable collection of accurate information of the field or farm in real time [2]; such information can be used to drive subsequent agricultural optimizations or interventions in the field.

As a WSN typically operates in a long-term, continuous mode, available energy resources become one of the most crucial challenges. This problem is exacerbated by the need for periodic data collection, node-level or cluster-level data processing, and data communication over the potentially long distances between the sensor nodes and gateways or base stations [1], [3]. Such subsurface sensor networks are often expected to operate without human intervention; however, in many applications, they are expected to be deployed in areas away from convenient access to the established energy grid. Although conventional on-board energy sources could be used to power these sensors, it would be time-consuming and costly to re-collect the sensing systems after the functional lifetime of the sensors has expired, or to replace the energy sources once they are depleted. One solution to this problem is onboard energy sources that can power the subsurface sensors during their functional lifetime, and passively degrade in an environmentally benign fashion after use or exhaustion. Our goal is to develop such long-lifetime, biodegradable, primary energy sources (biodegradable electrochemical cells, or 'biodegradable batteries'), and assess their performance in in-soil conditions.

Selection of the active materials of a conventional battery is mainly based on their performance and electrochemical stability. In contrast, the material requirements for biodegradable batteries are more stringent, considering that not only do the batteries need to exhibit good electrochemical performance and stable output over the operation lifetime, but have the additional constraint of passive degradation into nontoxic products, especially in agricultural settings [4].

Metal-air batteries have attracted significant attention due to their high theoretical energy density and high specific capacity

compared to commercial Li-ion batteries. A typical metal-air battery comprises a metal anode and an air cathode (normally comprised of a gas diffusion layer and a catalyst layer) [5]–[7]. The anode and cathode are separated by an electrolyte. The metal is oxidized into metal ions at the anode, while oxygen from the ambient air is absorbed and reduced to hydroxide ions in presence of H₂O at the cathode. In such batteries the oxidant is not stored within the battery volume but instead is extracted from the ambient; this approach enables high energy density, a more compact battery structure, and the potential for reduced environmental impact of the battery (since less material is introduced at the cathode side).

Among the metal-air batteries, Zn-air, Li-air, Al-air and Mg-air have been widely researched [8]. Of this materials set, Mg and Zn are the most popular biodegradable metals previously utilized in transient batteries [4], [9]. Though Mg-air batteries have higher theoretical capacity, their large polarization and high self-corrosion rates make them less favorable for long term applications [10]. Zn-air batteries are a very promising power source for biodegradable sensing systems, due to their high theoretical specific energy density (1084 Wh/kg), abundance of raw materials, safety, low cost, flat discharge voltage, and relatively low corrosion rate [7].

In addition to anode materials, the packaging, electrolyte/separator, and cathode must also be considered. For the package, blends of natural waxes such as those derived from soy and beeswax have been reported as slowly biodegradable hydrophobic encapsulants for soil moisture sensors by Sui et al. [11]; such waxes protected the sensor for an extended functional lifetime in soil. Simultaneous ecotoxicity tests suggested that these waxes do not hinder the growth of maize. For the separator, the biodegradable and water-soluble polymer poly-(vinyl alcohol) (PVA) can be formed into a hydrogel that functions both as the host of an alkaline electrolyte as well as a separator for Zn-air batteries. The fabrication process for such electrolytes was reported in our previous work [12]. For the cathode, commercially-available Platinum (Pt) loaded air cathodes can be considered, especially for laboratory testing. Ultimately, functional carbon electrodes, including nanostructured carbon and doped carbon, may be lower cost alternatives to Pt-loaded cathodes [13].

Air batteries are typically characterized in air or oxygen [14], [15]. For this application, we will investigate wax-packaged Zn-air batteries buried in soil. Week-long subsurface lifetimes of batteries have been achieved. Preliminary characterization of Pt-free carbon paper cathodes, typically used as a gas diffusion layer for fuel cells, suggests the carbon-based materials can be promising replacements of Pt cathodes for low-power long-term application.

EXPERIMENTAL

Active battery components: For anodes, commercial zinc foils (99.9% pure, 250 μ m, Sigma Aldrich) were patterned into disks with strip using an IPG Microsystem IX-200-F green laser (532nm). The disk is 1 cm diameter and comprises the electrochemically active area of the anode, while the strip is utilized for external electrical connection. For air cathodes, commercial Platinum Black paper (4 mg cm⁻² loading, Fuel Cells Etc.) and carbon paper (Sigracet 22 BB, Fuel Cells Etc.) were purchased and cut into 1 cm diameter discs using a hollow steel punch. Hydrogel electrolyte sheets were fabricated by solution-casting followed by rehydration [2]. 1.5 mg PVA (87-89% hydrolyzed, high molecular weight, Alfa Aesar) was first dissolved in 10 g of deionized water at 85°C. An

alkaline solution was prepared by dissolving 1.5 g KOH and 0.64 g K_2CO_3 in 10 g deionized water. After cooling both solutions, the alkaline solution was added to the PVA solution dropwise. The resultant PVA-KOH- K_2CO_3 precursor was then cast onto a glass petri dish, dried in a desiccator, and immersed in saturated KOH- K_2CO_3 solution for more than 2 days. After gel removal from the rehydration solution, discs with a diameter of 1.27 cm were cut from the gel using a second hollow steel punch (this slightly larger gel disc area prevents any short circuit contact between anode and cathode). Gel discs of different mass and thickness were realized by controlling the amount of the precursor used in the gel casting stage.

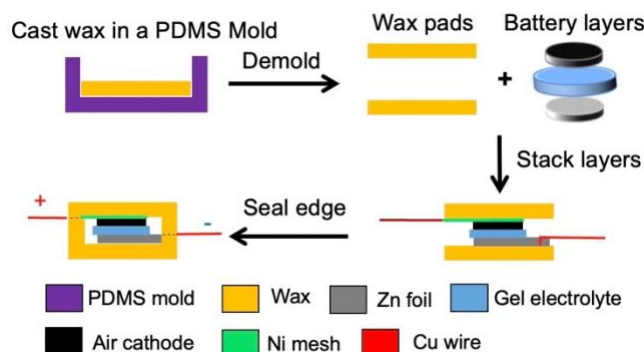


Figure 1: Cross-section of the fabrication process.

Assembly and Packaging: Figure 1 illustrates a cross-section of the wax encapsulation and packaging process. Two types of wax encapsulated batteries, with and without airholes, were fabricated using this method. The preparation of the wax itself is adopted from [11]. Beeswax and soy wax were mixed in a 1:3 mass ratio, melted at 80 °C, and cast in a PDMS mold (10:1 pre-polymer/curing agent, cured at 80 °C). The top and bottom encapsulation pads were demolded after solidification at room temperature. Open airholes were optionally introduced to the top wax pad (the one closest to the cathode side) by using a needle to punch through the pad. The three functional layers of the battery were then sandwiched between the pads, with a thin layer of Ni mesh contacting the cathode side to facilitate testing. Both Ni mesh and anode handle were attached to insulated Cu wires by silver paste for secure external connection. Finally, the four edges of the two pads were manually sealed by melted wax with interconnects enclosed to avoid parasitic leakage current when the battery is discharged in soil.

Reference batteries without packaging were also tested using a clamp board technique. Pairs of acrylic clamp boards with a porous structure in one board were fabricated by CO_2 laser machining and used to immobilize the active battery stack; a pair of screws extending between the boards could be tightened to clamp the active stack together.

Referring to Figure 2, Figure 2(a) shows a schematic of the wax-encapsulated battery, and Figure 2(b) shows the detail of how the nickel mesh structure is attached to the battery cathode. The remaining figures show wax encapsulated batteries with and without air holes, as well as a typical clamp board reference battery.

Test environments: To characterize in-soil performance, the batteries were placed in organic raised bed soil (Harvest Organics, Lowe's) inside 600 mL beakers at a controlled buried depth of 5 cm. Figure 3(a) shows a wax encapsulated battery in a beaker half-filled with soil. After the battery was placed, extra soil was placed on top until the desired depth is reached as shown in Figure 3(b). Copper wires extend from the buried battery to the anodic and cathodic clips of a battery cycler. Batteries of similar packages and gel masses were also tested in the air as references to the in-soil-tested devices.

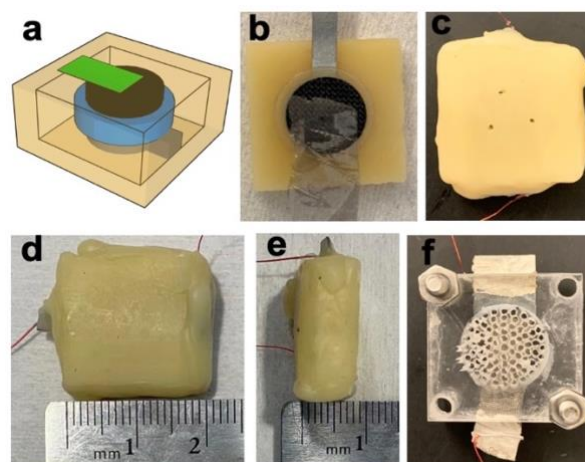


Figure 2: (a) Schematic of wax encapsulated Zn-air battery, (b) top view of a battery on a wax pad, (c), (d) top views of wax encapsulated batteries with and without airholes, (e) side view of a battery with wax package, (f) top view of a clamp board battery.

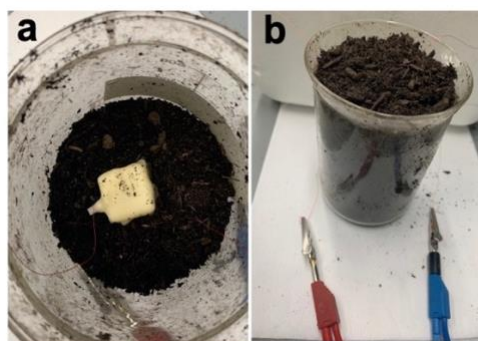


Figure 3: (a) Top view of a battery tested in soil, (b) front view of battery soil test set-up.

Performance characterization: Electrochemical assessment was performed using a BioLogic BCS-805 Ultra-Precision battery cycler. A 10-minute open circuit potential test was first carried out to stabilize the batteries in their respective environments. A current-voltage (I-V) curve to demonstrate the power capability of the battery was then performed through a galvanodynamic test with a scan rate of 5 mA/s from 0 to 100 mA. Battery performance was then characterized by chronopotentiometry testing. Batteries with Pt loaded cathodes were discharged at 30 μA , which is selected based on the power requirements of both MEMS fabricated oxygen sensors as well as RFID chips [16], [17]. A higher discharge current of 1 mA was utilized when characterizing the carbon paper cathodes to understand their catalytic performance in the absence of Pt. A typical 0.9 V cut-off voltage was taken as an endpoint of battery operation.

RESULTS AND DISCUSSION

A notable characteristic of air batteries is that their need to access ambient oxygen typically requires some degree of exposure to the environment. The performance of the battery may therefore be significantly affected by multiple variables in its operating environment. To assess these effects, batteries were characterized in multiple environments (air, 5cm deep in soil) and with multiple degrees of environmental exposure (clamp board, wax package with air holes, wax package with no holes) as shown in Figure 4. In these tests, the gel electrolyte mass was held constant at 38 mg to

eliminate the effect of the amount of gel.

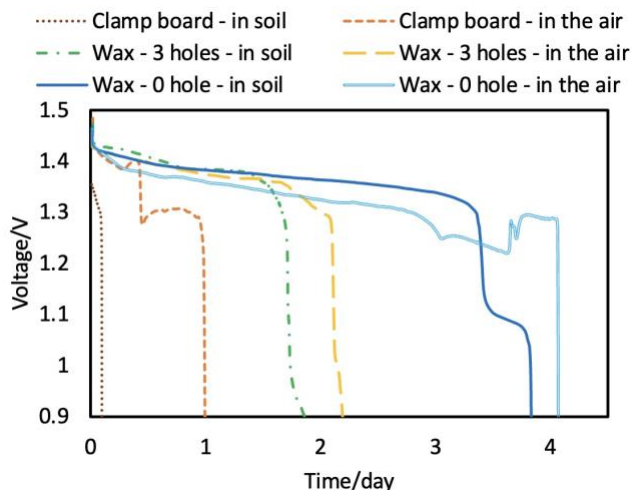


Figure 4: Discharge curves of batteries in various packages in the air and in soil.

The lifetime of the batteries discharged in the air were longer than the ones in soil for all three types of packages. This might be due to the influence of the soil condition. Soil is a porous structure containing solid particles, water and gas [18]. The relative humidity of the soil gas is close to 100% which is much higher than the air [19]. The alkaline electrolyte could absorb more water from the ambient environment when the battery is buried under soil, which could possibly lead to lower concentration of the OH^- in the gel electrolyte. As the solubility of intermediate zincate ion product at the anode side reduces with decreased pH, the zincate ion might reach the supersaturation point earlier and decompose to ZnO , resulting in more rapid passivation of the anode [15].

Another potential mechanism behind the variation of the lifetimes of batteries is carbonation. The OH^- ions in the hydrogel provide the ionic conductivity for the battery. While theoretically no OH^- will be consumed in the overall reaction, CO_2 in the air can diffuse together with O_2 into the battery, and react with the OH^- ions in the alkaline electrolyte to form CO_3^{2-} or HCO_3^- , which have much higher ionic resistivity than OH^- [20]. Since the amount of gel electrolyte is a relatively small 38 mg, the OH^- could be consumed gradually over time (as well as the electrolyte pH falling over time) as the battery discharges. When the concentration of OH^- falls too low, the reduced ionic conductivity can induce a large overpotential, leading to the end of discharge.

Clamp board batteries are the most vulnerable to such environmental variables, since CO_2 and moisture can access the battery not only from the maximally exposed porous structure at the cathode side, but also from side openings. It was thus not surprising to observe that the discharge lifetime of the clamp board batteries was the shortest. Wax-encapsulated batteries with air holes sustained a much longer discharge lifetime, perhaps due in part to the hydrophobic nature of the waxes, which results in extremely low water vapor permeability [21], as well as increased mass transfer limitations between the ambient and the porous cathode.

The wax-encapsulated battery with no air holes provided the longest lifetime both in the air and in soil. This might be due to its minimal exposure to the CO_2 and water vapor in the air and soil gas. However, the question of how these air batteries can function with no nominal air path should be addressed. One possibility is that even though there are no nominal air paths to the ambient, imperfections in sealing result in parasitic air paths sufficient to sustain battery

discharge. Another possibility comes from noting that even though the wax has low water vapor permeability, it is permeable to oxygen [21]. The long continuous discharge suggests that even with no nominal air holes, these mechanisms can sustain the low discharge current of $30 \mu\text{A}$ and fulfill the power requirement of the subsurface sensors.

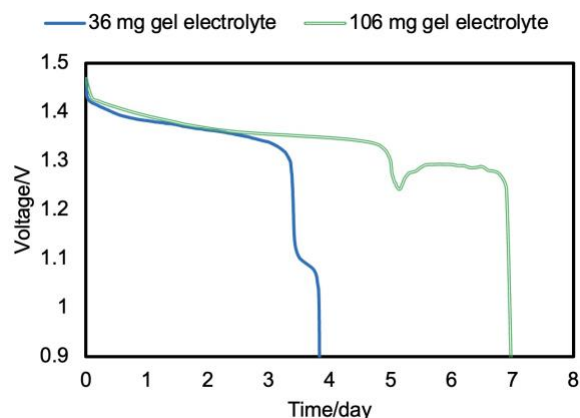


Figure 5: Discharge curves of wax encapsulated batteries (no hole) with different gels in the soil environment.

Since batteries fully encapsulated in wax with no nominal air holes result in superior discharge performance over other packages both in the air and in soil, this geometry was chosen to determine the effect of gel electrolyte mass on battery lifetime. As shown in Figure 5, an increase in the gel mass from 36 mg to 103 mg resulted in an 80% increase in battery discharge lifetime, supporting the hypothesis that the gel electrolyte can limit the performance of the batteries when its mass is low. Remarkably, the fully wax-encapsulated battery with 103 mg gel electrolyte provided a constant output voltage of over 1.2 V for 7 days in soil under a constant $30 \mu\text{A}$ discharge current.

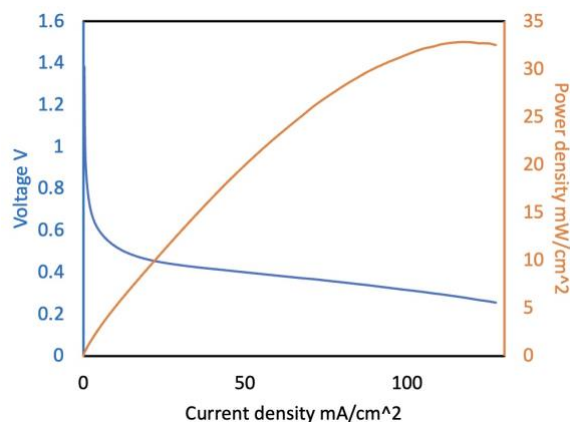


Figure 6: Power curve of the carbon paper cathode with 80 mg of gel electrolyte.

For cost considerations, we have also investigated replacing the air cathode bearing a Pt catalyst with commercial carbon fiber paper. Pt is a traditional oxygen reduction reaction catalyst that has high activity. A concern with replacing Pt with carbon is that the relatively low catalytic activity of carbon would lead to a higher energy barrier for the cathodic reaction and poorer power performance of the air battery [13]. However, it is also noted that in many of these WSN applications, low power output is acceptable.

As an initial test, a carbon-paper cathode material (Sigracet 22 BB) was tested with 80 mg gel electrolyte and clamp boards in air. This cathode material has a bilayer structure that consists of carbon fiber paper support and a carbon micro-porous layer. A galvanodynamic scan of this battery was performed to assess its power output as shown in Figure 6. Benefitting from the high surface area of the microporous layer, the peak power of the carbon paper clamp board battery is 32.9 mW/cm^2 , much higher than the tens of μW needed for sensor operation.

Figure 7 shows the discharge profile of the clamp board carbon paper battery. The working voltage of the battery exceeds 1 V under a relatively large discharge current of 1 mA, illustrating that the carbon cathode alone has sufficient catalytic activity for WSN applications at even at higher discharge rates. These results indicate the utility of carbon cathodes in these applications, as well as the potential of Zn-air batteries as biodegradable power sources to sustain long-term operation in subsurface conditions.

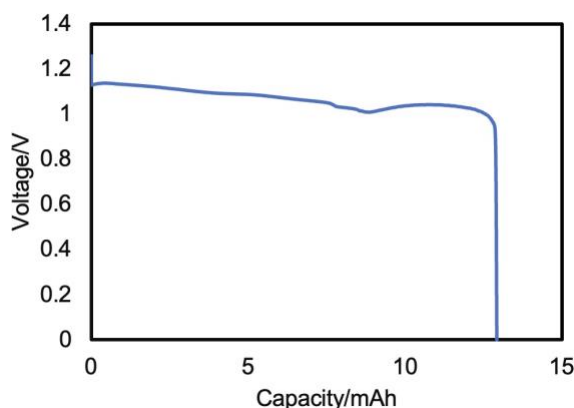


Figure 7: Discharge profile of a battery with a carbon paper cathode at a constant discharge current of 1 mA in air.

CONCLUSIONS

We present the materials and designs of Zn-air batteries with biodegradable package and gel electrolyte. The performance of the batteries with wax and clamp board in the ambient air and in soil environment are characterized by $30 \mu\text{A}$ constant current discharge. Biowax encapsulation are found to be functional packages both in air and in soil. A wax-encapsulated Zn-air battery with 103 mg gel electrolyte discharged over a week in soil at 5 cm depth. Carbon paper cathodes were also tested and shown to have sufficient catalytic activity for these WSN applications. We believe these results show the potential of Zn-air batteries as biodegradable power sources to sustain long-term operation in subsurface conditions for agricultural applications.

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REFERENCES

- [1] P. Corke, T. Wark, R. Jurdak, W. Hu, P. Valencia, and D. Moore, "Environmental wireless sensor networks", in

- Proceedings of the IEEE*, 98, 11 (2010).
- [2] H. M. Jawad, R. Nordin, S. K. Gharghan, A. M. Jawad, and M. Ismail, "Energy-efficient wireless sensor networks for precision agriculture: A review", *Sensors (Switzerland)*, 17, 8 (2017).
- [3] S. Sharma, R. K. Bansal, and S. Bansal, "Issues and challenges in wireless sensor networks", *Proceedings - 2013 International Conference on Machine Intelligence Research and Advancement, ICMIRA 2013*, 2014.
- [4] N. Mittal, A. Ojanguren, M. Niederberger, and E. Lizundia, "Degradation Behavior, Biocompatibility, Electrochemical Performance, and Circularity Potential of Transient Batteries", *Advanced Science*, 8, 12 (2021).
- [5] N. Chawla, "Recent advances in air-battery chemistries", *Materials Today Chemistry*, 12 (2019).
- [6] V. Caramia and B. Bozzini, "Materials science aspects of zinc-air batteries: A review", *Materials for Renewable and Sustainable Energy*, 3, 2 (2014).
- [7] J. S. Lee et al., "Metal-air batteries with high energy density: Li-air versus Zn-air", *Advanced Energy Materials*, 1, 1 (2011).
- [8] Md. A. Rahman, X. Wang, and C. Wen, "High Energy Density Metal-Air Batteries: A Review", *Journal of The Electrochemical Society*, 160, 10 (2013).
- [9] X. Jia, C. Wang, C. Y. Lee, C. Yu, and G. G. Wallace, "Energy materials for transient power sources", *MRS Bulletin*, 45, 2 (2020).
- [10] T. Zhang, Z. Tao, and J. Chen, "Magnesium-air batteries: From principle to application", *Materials Horizons*, 1, 2 (2014).
- [11] Y. Sui, M. Atreya, S. Dahal, A. Gopalakrishnan, R. Khosla, and G. L. Whiting, "Controlled Biodegradation of an Additively Fabricated Capacitive Soil Moisture Sensor", *ACS Sustainable Chemistry and Engineering*, 9, 6 (2021).
- [12] V. Venkatesh, Q. Yang, J. Zhang, J. Pikul and M. G. Allen, "Fabrication and Characterization of Evaporated ZINC Anodes for Small-Scale ZINC-Air Batteries", 2021 21st International Conference on Solid-State Sensors, Actuators and Microsystems (Transducers), (2021), pp. 1134-1137
- [13] Z. L. Wang, D. Xu, J. J. Xu, and X. B. Zhang, "Oxygen electrocatalysts in metal-air batteries: From aqueous to nonaqueous electrolytes", *Chemical Society Reviews*, 43, 22 (2014).
- [14] Y. Wei, Y. Shi, Y. Chen, C. Xiao, and S. Ding, "Development of solid electrolytes in Zn-air and Al-air batteries: From material selection to performance improvement strategies", *Journal of Materials Chemistry A*, 9, 8 (2021).
- [15] J. Stamm, A. Varzi, A. Latz, and B. Horstmann, "Modeling nucleation and growth of zinc oxide during discharge of primary zinc-air batteries", *Journal of Power Sources*, 360 (2017).
- [16] D. She and M. G. Allen, "A micromachined freestanding electrochemical sensor for measuring dissolved oxygen", *Journal of Microelectromechanical Systems*, 28, 3 (2019).
- [17] "https://www.nxp.com/docs/en/data-sheet/SL3S1003_1013.pdf."
- [18] "https://earthsoils.com/soil-composition/."
- [19] "https://www.doctordirt.org/teachingresources/idealsoil."
- [20] G. Li et al., "Carbonation effects on the performance of alkaline polymer electrolyte fuel cells", *International Journal of Hydrogen Energy*, 40, 20 (2015).
- [21] G. Donhowe and O. Fennema, "Water vapor and oxygen permeability of wax films", *J Am Oil Chem Soc*, 70, 9 (1993).

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