Single-Step S/N-Doped Biochar from Banana Peel as green catalyst for Water-Splitting

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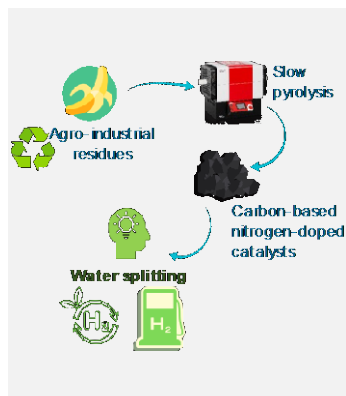
Electrochemical water-splitting process has been proposed lately as an alternative for the attainment of green H_2 as a renewable energy source. Nonetheless, the cost of this process is still too high to be relied on. Thus, research is required in order to synthesize catalysts which compete with the pollutant, expensive and unstable benchmark catalysts (IrO_2 and Pt/C). This research is based on the utilization of agro-industrial residues, namely banana peels which after their pyrolysis treatment showed catalytic activity on water-splitting. Moreover, doping with S and N the biochars enhanced the results thanks to the introduction of additional functional groups. Additionally, other factors such as catalyst concentration and the pH level of the solution were evaluated. The optimal catalyst showed a competitive performance and remarkable stability.

Introduction

The concept of a hydrogen-based economy is pivotal for the sustainable production, transportation, and storage of renewable energy, playing an integral role in driving the energy dynamics of the coming era. Electrochemical methods for generating hydrogen from the electrochemical cleavage of the water molecule typically rely on costly catalysts like IrO_2 and Pt/C, prompting the search for accessible and high-performing substitutes for these noble materials.

Carbon-based catalysts, devoid of metals, not only have revealed the potential to replace metallic catalysts but also offer an opportunity for sustainable production using agro-industrial residues. Materials such as orange peel, rice husk, and wood from invasive species can be transformed into high-value, carbon-based catalysts. This method is in line with zero-waste principles and the circular economy, which emphasize the reuse of waste materials to minimize environmental impact and enhance resource efficiency. By leveraging these abundant and often underutilized organic resources, we can move towards more sustainable and eco-friendly catalytic solutions. Thus, these agro-industrial residues can be thermally treated by pyrolysis attaining the so-called biochar, a porous and N/O-rich molecule which can be assessed for different catalysis and adsorption purposes [1]. Nevertheless, carbon-based catalysts typically exhibit lower catalytic activity compared to their metallic counterparts, the adaptable surface of biochar allows for modifications to its electronic structure, thereby improving its catalytic functionality [2]. Doping biochar with S and N enhances its electrocatalytic properties by altering the carbon matrix's electronic structure, increasing conductivity, and active sites availability. These changes result in improved charge transfer, greater electrocatalytic activity through functional group variation, and enhanced material stability. Consequently, such modifications significantly boost biochar's performance in applications like water electrolysis, making it a more effective catalyst [3]

Our research introduces a method for converting banana peel waste into a viable S/N co-doped biochar via slow pyrolysis, creating a metal-free catalyst for electrolytic water-splitting, focusing on the rate limiting step, the oxygen evolution reaction (OER). This methodology aligns with circular economy principles while offering a greener, more affordable catalyst option for water electrolysis.

Material and Methods

Banana biochar (BC) was synthesized at a pyrolysis temperature of 550°C over a period of 4 h, with the doping process incorporated into this single step. For that, N_2 gas inlet was fixed at 2 L/min. For the S/N doping process, various levels of thiourea were incorporated, with percentages by weight relative to the biochar as follows: 2.5%, 5%, and 10% (2.5%-S/N@BC, 5%-S/N@BC, 10%-S/N@BC).

The OER experiments were performed in an Autolab PGSTAT302N electrochemical workstation with an FRA32M analyzer. A three-electrode system was employed, featuring an Ag/AgCl reference electrode, a platinum wire counter electrode, and the catalytic working electrode. This electrode was prepared by first mixing 5 mg of S/N-doped biochar with 50 µL of a conductive Nafion ionomer solution (5% in aliphatic alcohols and water) and 1 mL of ethanol. This mixture underwent ultrasonic dispersion for 5 min followed by vortex mixing for attaining a uniform suspension. The resultant ink was applied to a 1 cm × 1 cm nickel foam

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piece, using 20 μL increments and hot air to speed up solvent evaporation between applications, until the electrocatalyst's desired mass evenly covered the foam's surface area.

Cyclic voltammetry (CV) was conducted at 5 mV s⁻¹ within 0-0.74 V in this three-electrode set-up in a 1.0 M NaOH electrolyte. Electrochemical impedance spectroscopy (EIS) was measured across 10^6 to 10^{-2} Hz for overpotential η10 with a 10 mV sinusoidal perturbation. Electrochemical Active Surface Area (ECSA) was measured by the realization of CV at different scan rates.

Chronopotentiometry and Accelerated Degradation Tests (ADT) were done to validate the stability of catalysts within, respectively, 100 h at 10 mA and 8,000 cycles.

Results and Discussion

BC exhibited water-splitting activity, increasing the electrochemical performance compared to the raw support Ni-foam (Figure 1), where it is noticeable that 5%-S/N@BC required the smallest overpotentials for attaining 10, 50 and 100 mA.
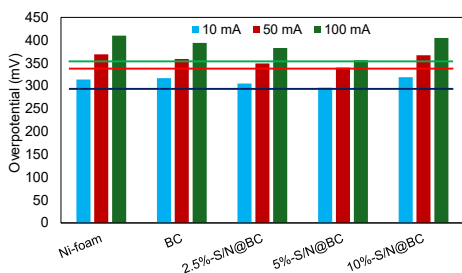
Figure 1. Overpotential comparison of the produced biochars.

Nevertheless, thiourea addition at different ratios for the synthesis of doped BC catalysts (S/N@BC), provided superior results (Figure 1), except when an excessive amount of thiourea (10%) was added. In this case, the thiourea clogs the pores of BC, reducing the ECSA (Table 1). ECSA values are related to the higher electro-catalytic activity [4].Further characterizations demonstrate that thiourea doping enhances the electrocatalytic activity. Indeed, EIS

provided information about the electron movements within the materials. Thus, a smaller semi-circle showed better conductivity (Figure 2). Specifically, series and parallel resistances (Rs and Rp, respectively) are provided. The smaller these values, better electrochemical set-up (Rs) and a higher electron movement (Rp) are present [4].
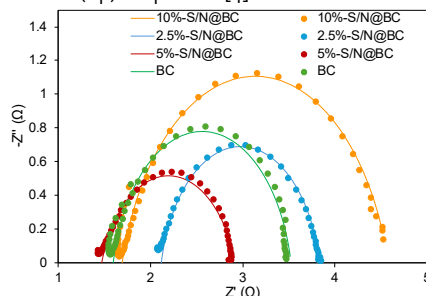
Figure 2. EIS analysis and simulated circuit (lines) of the biochars.

Lastly, the tafel slope which is related to the OER kinetics also confirms that 5%-S/N@BC represents the optimal catalyst, yielding the smallest tafel slope value.

Table 1. Electrochemical analysis of the synthesized biochars.

Sample	ECSA (μF/cm⁻²)	Rs (Ω)	Rp (Ω)	Tafel slope (mV/dec)
BC	30	1.6	1.92	86.7
2.5%-S/N@BC	20	2.12	1.72	85.84
5%-S/N@BC	37.5	1.47	1.45	80.8
10%-S/N@BC	31.4	1.69	2.89	93.6

Consequently, the optimal catalyst was evaluated in terms of stability, getting less than 10% detriment after chronopotentiometry 100 h treatment. Moreover, after ADT, the 8,000 CV even caused a 6% enhancement due to catalyst activation through activation.

All of this demonstrates that the attained metal-free 5%-S/N@BC catalyst can compete with benchmark catalysts.

Conclusions

The S/N co-doped biochar enriched with 5% thiourea displayed exceptional efficacy in alkaline media for oxygen evolution. The required overpotentials to attain current densities of 10, 50, and 100 mA were recorded at 287.7, 322.08, and 335.4 mV respectively, showcasing this catalyst's extraordinary performance. EIS and Tafel further confirmed the enhanced electronic attributes of this innovative material. Moreover, this catalyst showed remarkable long-term stability. These findings underscore the potential of S/N co-doped biochar as a competitive alternative to conventional water-splitting catalysts, paving the way for the broader implementation of such eco-compatible technologies.

References

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