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Development of metal free biochar based material for water electrolysis hydrogen production using anion exchange membrane: Creating circular economy

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ABSTRACT

In recent days, a steady growth is being noted in hydrogen energy field owing to the global rise in population and increased energy demand. Fast depletion of fossil-based fuels and climate change issues are driving nations towards exploring an alternate energy resource. Hydrogen energy is one such an option owing to availability of simple and cost intensive technology involvement. Alkaline water electrolysis is one of the simplest ways of producing hydrogen utilizing renewable energy and oxygen as the only byproduct thus not contributing to carbon footprint. However, immediate attention is needed to minimize the cost of electrolyzer components, maintenance and energy. Commercial proton exchange membrane water electrolyzers (PEM) in market employ large capital cost due to high-priced Nafion and other PFSA membranes, titanium endplates and noble metal-based electrocatalysts. As a consequence, researchers are looking into the usage of Anionic exchange membrane (AEM) for water/alkali based electrolyzer for producing hydrogen with non-noble metal electrocatalysts and low-cost metal end plates. In this article a waste coconut shell derived biochar is explored as the carbon matrix for base of electrocatalysts to replace other high-cost carbon support for electrocatalyst in water electrolyzer. The structural and electrical properties of the coconut shell biochar are studied and compared with other available carbon supports. To deep drive in the electrolyzer performance this approach is further extended to MEA (Membrane Electrode Assembly) level to study the metal free electrocatalyst behavior in real-time environmental conditions.

Keywords: hydrogen; anion exchange membrane; water electrolysis; biochar; electrocatalyst

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1. Introduction

1.1. Hydrogen, the next generation fuel

Abundant usage of fossil fuels causing heavy carbon footprints to the atmosphere leading to global warming worldwide. According to the latest report the rate of increase in temperature of earth’s surface in the last 40 years was doubled and since 1981 it increased by 0.18°C per decade. Consequently, Nation has to collectively agree on the issue of “carbon neutrality”/Net zero carbon. Another major problem that world encounter today is global energy crisis. Due to the surge in population, energy consumption as well as energy demand both are increasing. To meet net zero and to tackle energy crisis many nations are working to find an alternative source of energy which should be produced with zero carbon emissions or with less carbon emissions[1].

Hydrogen will be one of the best sustainable solutions which can be produced in a greener way when integrated with renewable energy sources like Solar Energy. Hydrogen economy has become a global phenomenon, because many countries believe that hydrogen can replace fossil fuels with certain modifications in automobiles and with a safer storage system. Hydrogen can be produced from various methods of resources and process methods each method with a varying greenhouse gas emissions, infrastructural requirements and cost[2,3]. Currently majority of hydrogen is produced from natural gas reforming i.e., 48% followed by different other sources as shown in **Figure 1**[3]**.** When it comes to hydrogen production processes using membrane technology, majorly there are three types of membrane-based technologies that are currently on to commercialization which includes 1) Solid oxide water electrolysis, 2) Proton exchange membrane electrolysis and 3) Anion exchange membrane electrolysis.

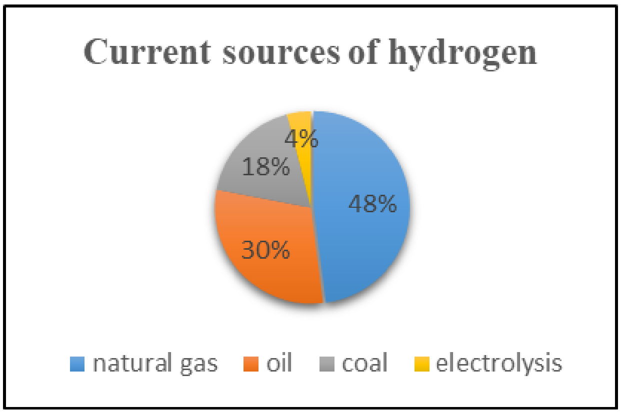


Figure 1. Current sources of H_2.

1.2. Potential of AEM technology

In 2023, Falcao et al. addressed the state of the art materials and technologies and demonstrated AEM water electrolysis as a future promising matured technology from the perspective of commercialization[4]. The drawbacks of PEM water electrolyzer include cost of membrane, acidic environment which demands expensive noble metal based electrocatalysts and electrolyzer components which are main bottlenecks in commercializing this technology. Researchers worldwide are in search of producing greener hydrogen in an economically viable way and several critical reviews on AEM water electrolysis technology are available in literature addressing the key focus areas such as membrane, electrocatalysts, MEAs etc.[5]. AEM technology has certain advantages like low cost membrane, cheaper SS materials can be used as bipolar plates, stability and durability of membrane electrode assemblies, non-noble metal catalyst supports instead of costly platinum group metals make the technology attractive and viable for scale up, however improvement of current densities with low applied potential, development of metal free electrocatalysts, purity of hydrogen and choice of flow fields are some of the R&D areas to explore further prior to commercialization.

1.3. Insights of AEMWE technology

1.3.1. Reactions involved

Common working principle of AEM water electrolyzer is to utilize alkaline water (KOH solution) which dissociates into hydroxyl ion and hydrogen molecule at cathode and this hydroxyl is transported back to anode through the AEM membrane where it evolves oxygen and water. The schematic illustration is shown in **Figure 2** and the electrode half-cell reactions are shown below:

Anode: $2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$ (1)

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (2)

Overall cell reaction: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ (3)

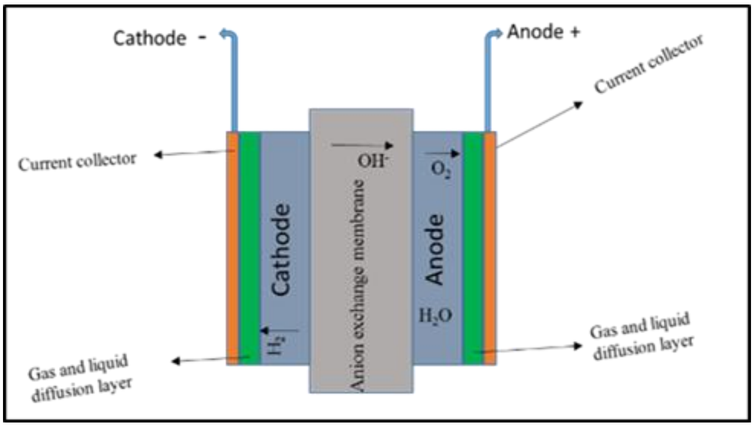


Figure 2. The schematic diagram of AEMWE.

1.3.2. Membrane, current collectors and electrocatalysts for AEM electrolyzer

Membrane is the most costly part associated in PEM water electrolyzer. Here polymer electrolyte membranes are used (Nafion: PFSA/PTFE backbone with sulfonic acid as functional group) which has a distinctive disadvantage of loosing proton conductivity under elevated temperature of water. AEM membranes are based on polymeric backbone with quaternary cations at the chain end. They are of relatively low cost and on high demand due to its mechanical/thermal stability and comparable electrical conductivity with PEM. In AEM water electrolyzer Nickel mesh as gas diffusion layer/current collectors are being used widely for its non-corrosive nature, good electrical conductivity and stability in alkaline medium. However, enhancement in current density and durability were observed with Nickel foam for its nano-porous structure[4,5].

Main cost cutting option for commercial hydrogen production is to synthesize non noble metal/metal free based catalysts support for MEAs in electrolyzers. Studies have been carried out worldwide to explore cheap and electrochemically active non noble metal based electrocatalyst in water electrolyzer for production of hydrogen[2,6]. Currently research is being done to synthesize carbon support from waste biomass and impregnation with hetero atoms (like Nitrogen, Phosphorus, and Boron & Sulphur etc.). Many attempts are being done not only to make noble metal free electrocatalysts[7–9], but also complete metal free electrocatalysts[10–12]. Since the first reported metal free carbon based electrocatalyst in 2009[13] the research for effective metal free electrocatalysts is increasing. However, in 2014 the first reported HER (Hydrogen Evolution Reaction) material was reported[14]. After this the new trend now is to generate useful materials from waste which is a sustainable approach for a better future is being studied. In this regard many materials are being reported as an energy storage and generation applications[15,16]. There are many publications related to biochar based materials for energy production applications are being reported[17,18]. Some of them reported the biochar and non-noble metal based water electrolysis application for H_2 production[19–22]. According to the Indian Trade Portal, India is one of the largest coconuts producing country in the world with a share of 31.45% of total world’s production. In this regard the conversion of the waste coconut shell, husk and other carbonaceous materials to useful materials creates the circular economy. Many attempts are being made to make use of coconut shell based biochar as a potential electrocatalyst for various energy conversion and storage technologies[17–22]. Coconut shell biochar is chosen in this study is due to its high carbon content in the range of 53–64% and also its low ash residue[23,24]. Even though previously reported methodology of coconut shell biochar gave good performance they are multistep processes and many chemicals are involved in the process[25,26]. The porous carbon derived from coconut shell biochar exhibits high surface area (800–1600 m^2g^{-1}) and also shows large number of mesopores and open pore structure, which makes the active sites available for electrochemical reactions[27,28]. In general, there are many factors that influence the final biochar based catalyst preparation such as pyrolysis temperature, activation agent and washing of prepared catalyst to remove impurities which expose the surface functional groups and pores. The choosing of coconut shell as a source of biochar for electrocatalyst application in this research stems from its elevated carbon content, diminished ash levels, and notable hardness, all of which confer advantageous attributes for its prospective utilization in electrocatalysis application[29]. This is due to distinctive morphological characteristics inherent to the plant cell structure of the coconut shell, characterized by densely interconnected cellulose, hemicelluloses, and lignin. Urea which is used in this study to dope the N is non-toxic and is less expensive compared with other precursors[27]. There are many types of activation methods conventional activation methods are physical activation and chemical activation[19]. Chemical activation is chosen in this study, where the impregnation of the activating agent along with the carbon and get pyrolysis done together in a single step rather than multi step as in physical activation method. Selecting the activating agent has to be done carefully to get desired properties to the biomass after pyrolysis based on the target application. There are many chemical activating agents, where KOH is chosen due to its less environmental impact and less expensive and the ability to create high surface area and pore volume to the carbon structure[30].

2. Materials and methodology

2.1. Synthesis of electrocatalyst

Coconut shell is a common tropical biomass which is easily available and can effectively be converted to biochar for wide applications. Recently there are many reports where the pyrolysis of biomass to biochar are reported which are multistep processes, where the pyrolysis of biomass to biochar is the first step followed by activation/modification of pristine biochar as second step. Multistep processes decrease the yield and also increase the cost at large scale production. To avoid multistep and simplify the process of producing N doped coconut shell biochar, hence followed single step pyrolysis of coconut shell. In lab, a dried coconut shell was broken into small pieces and washed thoroughly with distilled water and kept it for drying under sunlight for 48 hours. Dried shell pieces were kept for carbonization in a muffle furnace at 200°C for 2 hours. This step removed moisture leftover in the shell and CO_2. Then the material was grounded and sieved through a mesh size of 0.212 mm and thoroughly blended with urea and KOH in 1:2:2 weight ratio and loaded in a small quartz boat and was kept inside a in house pyrolysis unit. Nitrogen gas was purged continuously at a flow rate of 1–2 slpm (Standard liter per minute) creating inert atmosphere inside the unit and to control unwanted reactions. The temperature increased at a rate of 10°C per minute and maintained at 700°C for 2 hours. Conversion of biomass to biochar takes place by thermal decomposition at controlled conditions such as, in the temperature range of 260°C to 400°C, the breaking of C–O and C–C bonds within the ring units occurs, leading to the liberation of CO and CO_2. Simultaneously, de-polymerization and chain scissions processes are initiated. At temperatures above 400°C graphitic layers are formed. After that the unit was allowed to cool down and N_2 gas purging is stopped. After cooling down to room temperature the material was collected and washed with 1M HCL solution followed by water thoroughly, until neutral ph-7. The washing process involves the immersion of the activated carbon in a 1M HCl solution, facilitating the removal of impurities and amorphous carbonaceous residues from the carbon matrix[31]. Through this acid washing procedure, extraneous materials and contaminants were effectively leached away, leaving behind a purified carbon substrate. Importantly, this purification step plays a crucial role in exposing the inherent crystalline structure of graphite present within the activated carbon[32], and finally the sample is dried at 80°C in a vacuum oven for 24 hours. The temperature of the pyrolysis should not cross beyond 700°C, because study done by Chen et al. suggested that low temperature pyrolysis is more economical in retaining the surface functional groups and also high temperatures causes collapse of pores which ultimately decreases porosity[33]. The detailed procedure is illustrated in **Figure 3**.

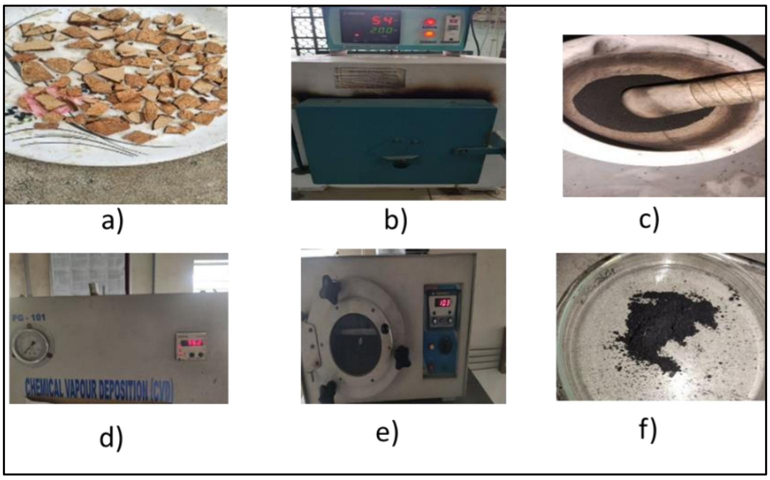


Figure 3. Step wise synthesis of Electrocatalyst material from coconut shell; **a)** Washing and drying of coconut shell pieces; **b)** Initial Carbonization in Muffle Furnace at 200°C; **c)** Grinding and mixing with urea; **d)** In house fabricated Pyrolysis unit; **e)** Drying out in an oven after washing; f) Final product.

2.2. Electrochemical characterization

Cyclic voltammetry studies were carried out in CH Instruments Inc. using a Glassy Carbon Electrode (GCE) (3 mm in diameter) as a working electrode, Saturated Calomel Electrode (SCE) was used as the reference electrode, and Pt wire served as the counter electrode, respectively. In a solution of 1M potassium hydroxide (KOH) where the electrolyte is N_2 saturated before the experiment.

2.3. Membrane pretreatment

Membrane pretreatment is an essential step for its performance and low resistance to charge transfer. Fumapem membrane (FAA-3-PK-130) was soaked in 0.5 M KOH solution for 24 hours at 30°C. Then it was thoroughly washed with deionized water and stored in desiccator/closed container to avoid moisture and CO_2 contamination.

2.4. Membrane electrode assembly

The carbon material prepared was suspended in a mixture of isopropyl alcohol and fumion® FAA-3 solution in NMP (10%) (Procured from fuel cell store) and water to form a homogenous ink. The same have followed for the IrO_2 (procured from Sigma Aldrich). The target loading on the membrane for both sides is 2 mg/cm^2. The catalyst ink is ultrasonically mixed for 60min and poured in a vessel of Air driven spray gun. The catalyst ink is sprayed on the membrane in the defined area. After drying of the membrane and was hot-pressed at 60 bar pressure and at 60°C temperature for 3 min using a pneumatic hot-press.

2.5. Operation of a single cell with anion exchange membrane

The single cell assembly of active area 10 cm^2 made up of stainless steel is used, where Nickel mesh is used as current collectors and as a gas diffusion layer. Silicon gaskets of thickness 1 mm is used to seal the cell with a torque of 9N-m. A DC voltage was applied and operated at current densities 0.1–1 A/cm^2. 1M KOH solution is chosen an electrolyte feed for as prepared electrocatalyst MEA and studied the empty membrane performance with both water and 1M KOH Electrolyte solution was supplied to the cell under gravity from both sides of the cell (cathode & anode). The performance was evaluated by current and voltage (I-V) characteristics curves generated during water electrolysis and hydrogen gas were measured by water displacement method. All experiments were carried out at 1 atm. pressure.

3. Results and discussion

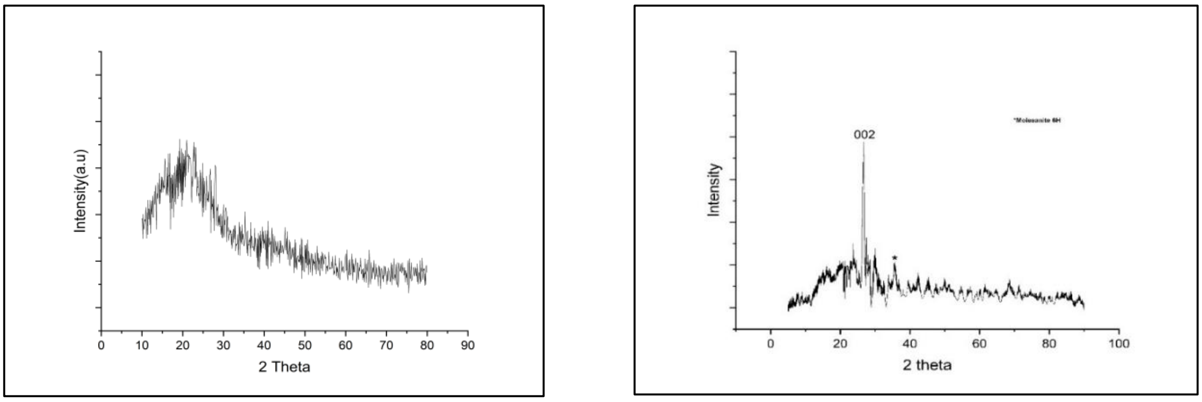
3.1. Physio-chemical characterization

Figures 4a and **4b** shows X-ray diffraction (XRD) patterns of pristine and N-doped coconut biochar respectively. XRD is a useful to differentiate the compositions and crystallinity of the synthesized materials. The peaks which are formed between 2θ = 20°–30° refers to aromatic graphitic layers which are stacked up together[6]. The sharp high intensity peak at 2θ = 26.6° confirms the crystalline graphitic carbon with (002) plane structure with a d-spacing of 0.33 nm which is similar to graphite structure interspacing. Usually value of $d_{(002)}$ is taken as degree of graphitization in the carbon larger values indicates the disorderness[34]. The other small peak at around 2θ = 35.6° refers to a mineral Moissanite 6H (SiC). There are other peaks of small intensity which are related to other inorganic materials of Si, Ca and K, which are the integral part of biochar. These impurities will definitely improve the electronic properties of biochar, for example, Liu et al. studied the effect of Fe particle impurities on oxygen evolution reaction[35]. The structurally modified coconut shell biochar exhibits a high degree of crystallinity characterized by a graphitic structure, as discerned from X-ray diffraction (XRD) analysis. This distinctive structural attribute renders it notably suitable for applications in electrocatalysis. The sp2-hybridized carbon atoms in graphitic carbon form a highly conductive network. This conductive pathway facilitates the efficient transfer of electrons during electrocatalytic reactions. In electrocatalysis, where electron transport is crucial, the presence of graphitic carbon enhances the overall electrical conductivity of the material[36]. Graphitic carbon demonstrates active catalytic sites, particularly concentrated at defects and edges within the graphene layers. These active sites assume a crucial role in both the adsorption and activation of reactant molecules throughout electrocatalytic processes. The presence of defects establishes sites for anchoring, thereby facilitating electrochemical reactions and contributing to an enhancement in the overall catalytic activity[37]. Graphitic carbon exhibits greater stability and durability compared to amorphous carbon structures. This is particularly advantageous in electrocatalysis applications where the material is subjected to repeated cycles of oxidation and reduction. The robust nature of graphitic carbon in prepared coconut shell biochar ensures a longer lifespan for the electrocatalyst.

From the XRD plots, the synthesized material was found to be mostly crystalline in nature compared to the pristine biochar. By virtue of this meticulous washing protocol, the resulting activated carbon material becomes enriched in graphitic content, enhancing the clarity and accessibility of its crystalline structure. The average crystallite size of the samples was calculated from major X-ray diffraction peaks using the Debye-Scherer's equation as shown in Equation (4), the calculated average particle size is 119.5 nm without any ball mill techniques.

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{4}$$

where D is the average diameter in nm, k indicates the Debye Scherer's constant (0.89), λ is the wavelength of X-rays (l ¼ 0.154 nm), β is the full width at half maximum (FWHM) of the diffraction peak and q is the Bragg's diffraction angle.

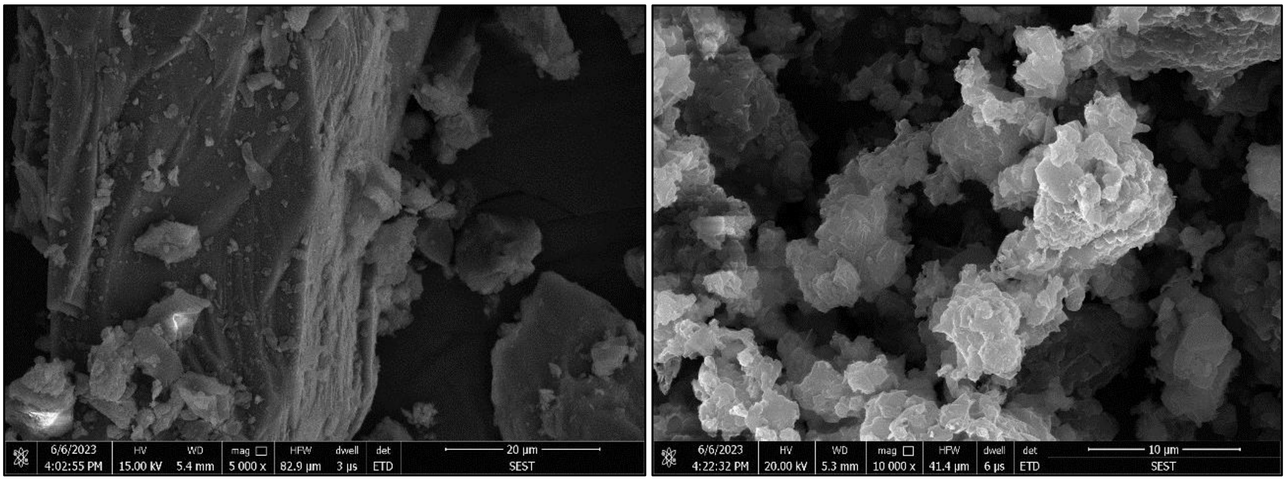


(a) **(b)**

Figure 4. XRD patterns of pristine and N-doped coconut shell biochar; **(a)** XRD patterns of pristine coconut shell biochar; **(b)** XRD patterns of N-doped coconut shell biochar.

3.1.1. SEM morphology

Figure 5a showing the SEM image of pristine coconut shell Biochar, which is prepared at the temperature of 200°C. The surface morphology shows large lumps of carbonaceous material with a bulk structure and is solid in nature. However, when the pyrolysis temperature is increased and effect of KOH and urea can be clearly seen in the **Figure 5b** which shows the flaky graphite structure, which are stacked up together as a sheet. Thus, the both activating agent and urea played their role not only in graphitization but also pores formation[38,39]. Urea which is used as a source of nitrogen doping also helped in more pore formation. Cheng et al. when used urea as an activating agent observed that more pores are formed because of urea addition during pyrolysis, these pore helps is effective mass transport. According to Zou et al. in the presence of the KOH activator, urea exhibits synergistic effects on the alteration of both pore diameter and surface area in the samples. The observed changes in porosity are primarily attributed to the liberation of gases, such as NH_3, resulting from the decomposition of urea.



(a) **(b)**

Figure 5. SEM images of Pristine biochar at 200°C and N-doped biochar at 700°C; **(a)** Pristine biochar at 200°C; **(b)** N-doped Biochar at 700°C.

3.1.2. Electrochemical characterization

As prepared catalyst, cyclic voltammograms are shown in **Figure 6**. CV was recorded between the potentials −1.2 to 0.2 at a sweep rate of 20 mV s^{-1}. These experiments show the electrochemical activity of prepared biochar carbon materials. The CV was recorded in the electrolyte solution of 1M KOH. In the **Figure 6**, one can clearly see the HER reaction at −0.2V vs SCE. However, simple biochar materials do not exhibit such type of peaks[34]. This is due to surface pores and active sites which expose functional groups of biochar to electro catalytic activity. And also due to nitrogen hetero atom which changes the electronic structure of a carbon material when doped. Hetero atom like Nitrogen doping proves to be an effective modulator of surface chemistry, electron-donor capacity, and electrochemical characteristics within the sp2 carbon structure. This is validated by both experimental observations and density functional theory (DFT) calculations[36]. Nitrogen-containing functional groups, such as pyridinic, pyrrolic, and graphitic nitrogen, introduce catalytically active sites on the biochar's surface. These active sites can facilitate and accelerate various chemical reactions, making nitrogen-doped biochar suitable for electrocatalytic applications. In addition, nitrogen atoms can stabilize active sites on the biochar surface, preventing the deactivation of catalytic centers. This stability is crucial for maintaining the long-term efficacy of the material in catalytic applications[40,41].

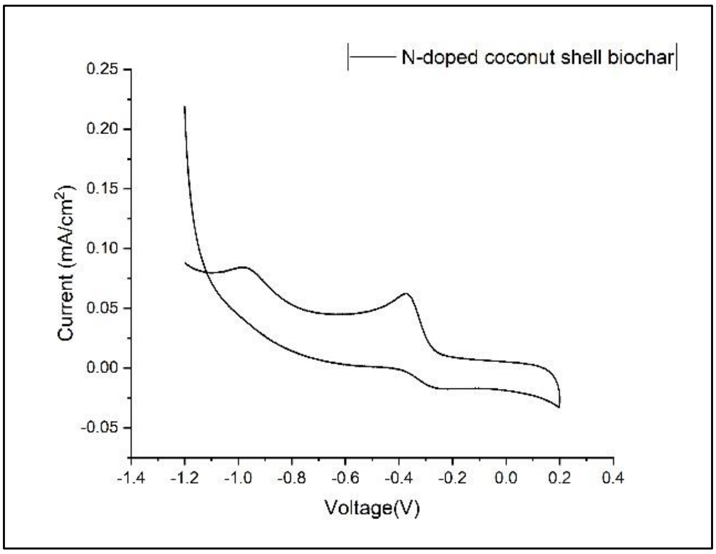
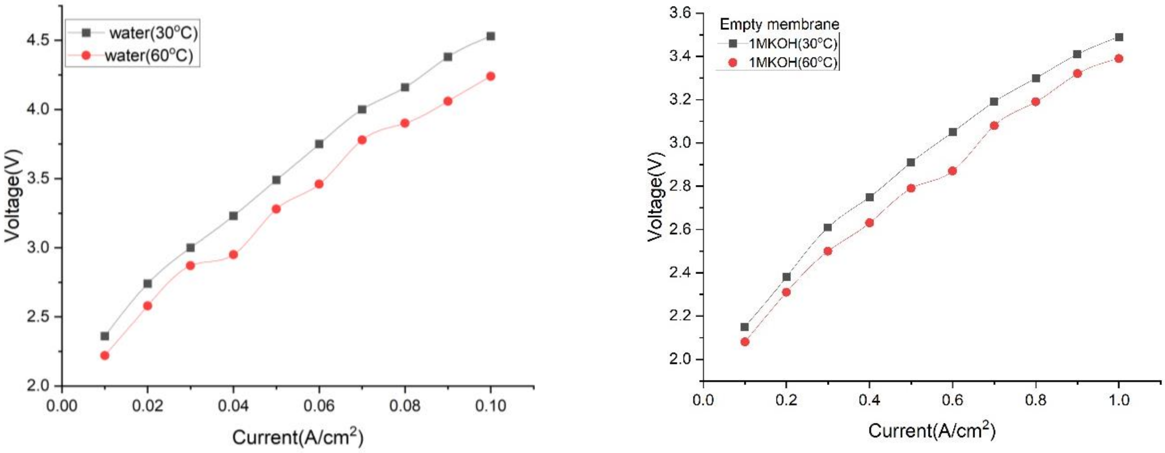


Figure 6. Cyclic Voltammograms of prepared N-doped coconut shell biochar.

3.2. Performance of AEM water/alkaline water electrolyzer

3.2.1. Performance of Empty Anion exchange membrane with deionized water and 1MKOH for 10cm2 cell area

The electrolysis performance of MEAs containing empty anion exchange membrane was studied. The performance using pure DI water and 1M KOH solution is studied. Typical steady state current-voltage polarization curves were recorded along with corresponding yields of hydrogen at different temperatures up to 60°C using the DI water, as shown in **Figure 7a** and with 1MKOH shown in **Figure 7b**. The cell voltage gradually decreased as the function of temperature up to 60°C with maximum current density up to 0.1 A/cm^2 in case of pure DI water and 1A/cm^2 in case of 1M KOH.



(a) **(b)**

Figure 7. Current-Voltage Polarization curves of the empty membrane with pure DI water and 1M KOH; **(a)** Current-voltage polarization curve of empty membrane with pure DI water at different temperatures; **(b)** Current-voltage polarization curve of empty membrane with 1M KOH at different temperatures.

3.2.2. Performance of N doped coconut Biochar coated Anion exchange membrane with Alkaline water for 10 cm^2 cell area

The performance of MEAs of 10 cm^2 containing empty anion exchange membrane was studied with 1M KOH with Nickel mesh as current collectors and compared with N doped coconut Biochar coated Anion exchange membrane with 1M KOH solution at different current densities up to 1.0 A/cm^2. The performance of MEAs coated with N doped coconut Biochar with 1M KOH solution was increased when compared with empty membrane with 1M KOH. The hydrogen yields were calculated and found that 34.1 ml/min at 0.5 A/cm^2 and 67.8 ml/min at 1 A/cm^2 as shown in table1. N doped coconut Biochar in Anionic exchange membrane Alkali water electrolysis polarization curves are shown in (**Figure 8**). The voltage at 0.1 A/cm^2 is measured as 1.98V. As observed, with the increase in temperature the voltage of the cell is decreased. This is due to weakened bonding of hydrogen present in water molecule at elevated temperature requiring less energy to break it. As higher voltages are not recommended because of possible catalysts degradation and hot spot formation, which will lead to catalyst layer leeching and membrane degradation and performance losses. Hence, the voltage efficiency should be improved by tuning the catalysts. The improved performance of N doped coconut shell biochar is due to crystalline graphitic structure and also the nitrogen atom which plays a crucial role in electron transfer. Studies done by Shiva et al, by doping different hetero atoms to carbon materials revealed the improved performance of the electrocatalyst[42–44].

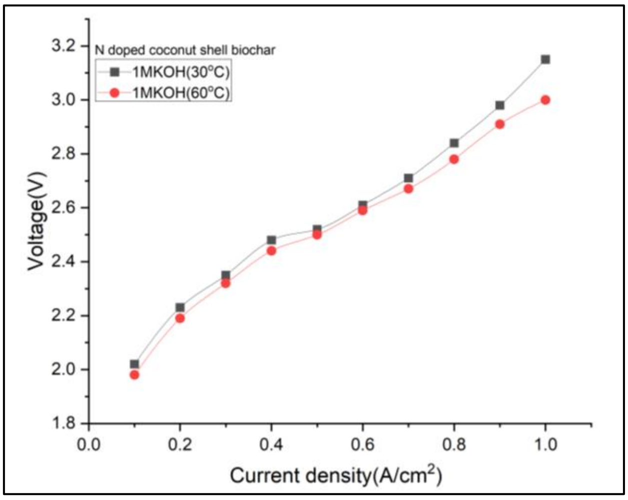


Figure 8. Current-voltage polarization curve at different temperatures with as prepared Cathode catalyst.

3.2.3. Hydrogen yield

Theoretical hydrogen production is calculated according to the second law of faraday[38]. And the experimental yield of hydrogen gas for as prepared N doped coconut shell biochar is calculated using water displacement method, from where the faradaic efficiency is calculated and mentioned in the **Table 1**.

Table 1. Hydrogen yield calculated for N doped coconut shell biochar Electrocatalyst.

S. No.	Experimental Hydrogen yield (L h^{-1}) 10 cm^2	Theoretical Hydrogen yield(L h^{-1}) 10 cm^2	Current Density mA/cm^2	Cell Voltage (V) at 60°C	Faradaic Efficiency
1	2.05	2.09	500	2.50	98.%
2	4.07	4.18	1000	2.98	97.3%

3.2.4. Hydrogen gas cross over

Hydrogen gas purity was measured using Endee GAP-2008 and the purity of hydrogen in the cathode chamber is 98.5% and observed nominal gas cross over hydrogen in oxygen side and the measured value is 1%.

4. Conclusion

Here biochar based electrocatalyst for AEMWE was prepared and studied, where one-step pyrolysis and activation method was chosen and doped with the nitrogen heteroatom to the pristine biochar. In this work, it is successful in developing graphitic structure that was confirmed by XRD and SEM results where many biomass based biochar materials show amorphous structure. Experimental conditions and washing of the final materials play a key role in exposing the crystalline structure of graphite. Catalyst behavior was tested on a MEA level as the cell electrode sometimes behave differently in real time conditions inside the cell. As the electrocatalyst performance is largely associated with other factors such as mass transfer through gas diffusion layer, ion transfer through membrane, porosity of membrane and binding capacity of catalyst materials to the membrane, it is essential to test the overall performance of the MEA assembly towards hydrogen production prior to conclude and comment on catalyst suitability and behavior in the cell. With this material achieved a current density of 0.1 A/cm^2 at 1.98V at 60ºC with the prepared metal free N doped biochar. There are still research going on how the cell performance in terms of current density and overall hydrogen production can be improved by heteroatom atoms such as S, B, P etc. and combination of other heteroatoms like N and P doping in carbon nanoparticles will improve the overall cell efficiency.

Author contributions

Conceptualization, HV and GKB; methodology, HV and GKB; formal analysis, GKB; investigation, GKB; resources, HV and SCCH; data curation, GKB; writing—original draft preparation, GKB; writing—review and editing, GKB and CR; visualization, GKB and CR; supervision, HV; project administration, HV; funding acquisition, HV. All authors have read and agreed to the published version of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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