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Sustainable electrodes based on biomass-derived catalysts and Ionomers for the Oxygen Reduction Reaction

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Abstract

Anion Exchange Membrane Fuel Cells (AEMFCs) are promising clean energy devices. To align their development with sustainability goals, this study explores the integration of biomass-derived components into AEMFC cathodes. Biochar-based electrocatalysts were synthesized via hydrothermal carbonization (HTC) of pine needles, a water-based, low-temperature process. Three processing strategies were investigated: direct HTC of raw biomass, HTC following biomass pre-treatment, and thermal post-treatment of the resulting hydrochar to promote graphitization. In parallel, a biomass-derived anion exchange ionomer (AEI) was synthesized via polycondensation of 2,5-furandicarboxylic acid with p-phenylenediamine, followed by reduction and quaternization. The resulting furan-based AEI was incorporated into the cathode and benchmarked against a PPO-based ionomer (PPO-LC). Electrochemical testing showed that the furan-based AEI led to lower performance, particularly fewer exchanged electrons, though onset potentials remained comparable to the Pt/C reference. Hydrochar derived from raw pine needles demonstrated favourable performance with minimal processing, avoiding organic solvents and lowering the energy demand. In contrast, a high temperature post-treatment offered only marginal performance gains at high energy cost, limiting its sustainability. This study highlights the importance of balancing performance, processing effort, and environmental impact in AEMFC electrode development.

Keywords Hydrothermal carbonization (HTC), Furan-based ionomer, Biochar, Sustainable electrode design, Electrocatalysis

1 Introduction

Anion Exchange Membrane Fuel Cells (AEMFCs) are expected to play a crucial role in the transition to a more sustainable energy economy, offering a clean method of energy conversion from renewable sources while reducing greenhouse gas emissions [1]. AEMFCs operate under alkaline conditions, which facilitates the use of non-precious metal catalysts; the alkaline environment enables faster oxygen reduction reaction (ORR) kinetics and potentially greater fuel flexibility [2, 3]. However, for AEMFCs to emerge as truly sustainable alternatives, it is not sufficient to focus solely on performance metrics.

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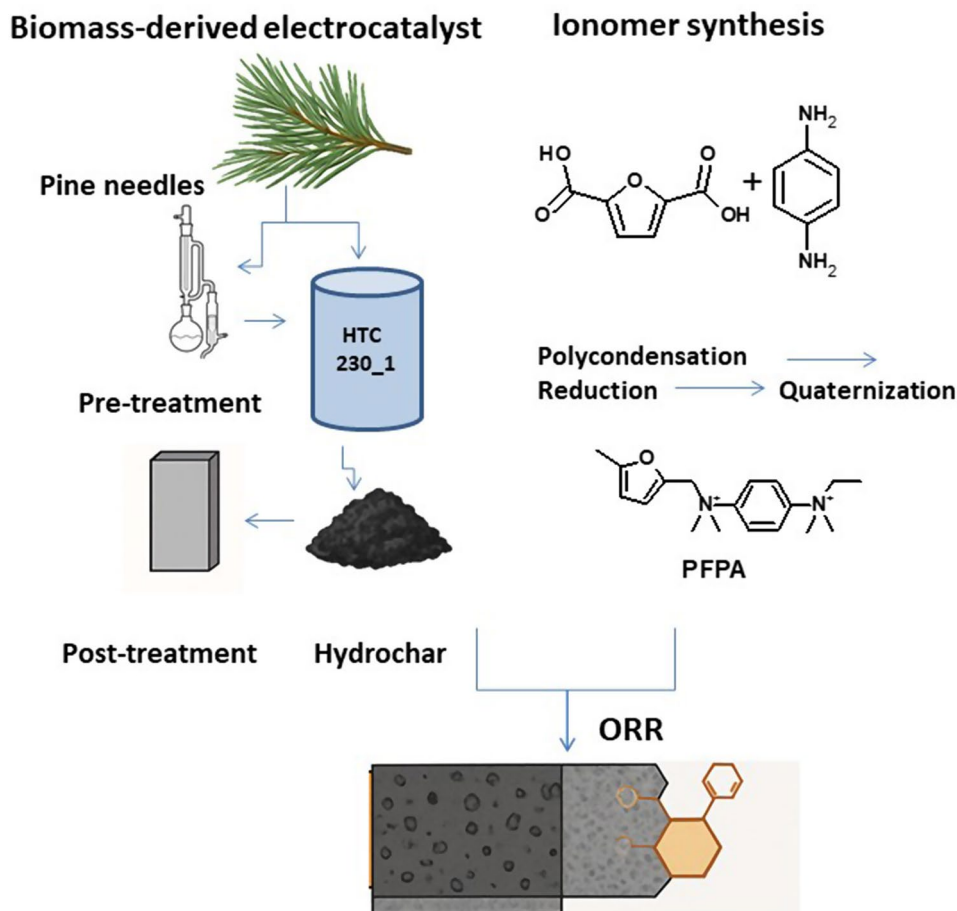
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Graphical Abstract



To ensure that the environmental benefits of renewable energy are fully realized, it is essential to move beyond performance alone and consider the sustainability of the materials used. This requires the development of Fuel Cell (FC) components made from abundant, accessible elements, and preferably produced from renewable raw materials through green and cost-effective processes. The main objective of this work is to initiate a sustainable approach to develop the components of catalytic electrodes for the ORR in AEMFCs. This includes the use of biomass-derived resources and alternative materials with a lower environmental impact.

Biochar, a carbon-rich product obtained from biomass, is gaining traction as a sustainable carbon source due to its low cost, reduced carbon footprint, and potential to support a circular economy [4, 5]. By introducing heteroatoms such as nitrogen or sulfur into the carbon matrix, biochar's catalytic properties can be significantly enhanced, making it suitable for application as a metal-free electrocatalyst for the ORR [6, 7]. Biochar can be produced by hydrothermal carbonization (HTC) of

biomass (hydrochar), leading to carbonaceous material with rich surface chemistry [8–10]. HTC is a low-temperature (150–350°C), water-based thermochemical conversion technique that mimics natural coal formation. It effectively decomposes biomass through hydrolysis, dehydration and decarboxylation reactions under sub-critical water conditions [11]. The resulting solid product typically contains a higher percentage of oxygenated surface functional groups, improving its hydrophilicity and chemical reactivity, important qualities for electrocatalytic applications [12, 13].

Despite these advantages, the use of hydrochar in electrochemical devices is still emerging, and extensive research is required to optimize its properties for fuel cell applications. One of the major enhancements involves nitrogen doping of nitrogen-poor feedstocks during HTC, which introduces nitrogen-containing functional groups (e.g., pyridinic-N, pyrrolic-N, graphitic-N) into the carbon lattice [14]. These species are known to enhance the ORR activity by modifying the electronic

structure, surface charge, and wettability of the carbon material [15].

In this study, we investigated and compared hydrochar materials derived from pine needles, applying various processing strategies to assess their impact on the final material properties. Specifically, we examined the effects of: (i) HTC following a pre-treatment of the biomass, (ii) direct HTC of raw pine needles (called waste hereinafter, W), and (iii) a subsequent thermal treatment at 800 °C of the resulting hydrochar (called post-treated hereinafter, PT). This high temperature process is intended to enhance the electronic conductivity through partial graphitization [16]. This comparative approach enables a deeper understanding of how pre- and post-processing steps influence the structure and the electrocatalytic performance of biomass-derived carbon materials.

Another critical component in the architecture of catalytic electrodes is the anion exchange ionomer (AEI) [17]. The AEI plays a dual role: it assures the mechanical cohesion ("binder") and it contributes to the formation of the triple-phase boundary (TPB), the interfacial region where gas, ionomer, and catalyst converge to enable efficient electrochemical reactions, enhancing the transport of OH⁻ ions [18, 19]. In our previous work, we observed that AEIs incorporating long side chains (LC) into a poly(phenylene oxide) matrix (PPO-LC) displayed superior ORR activity, delivering notable current densities [20]. However, despite their high performance, such materials are based on fossil-derived polymers, which raises concerns in the context of green chemistry and resource sustainability. In the present study, we propose a sustainable and innovative alternative: AEIs synthesized from biomass-derived model molecules. Among these, we selected 2,5-furandicarboxylic acid (FDCA) as a renewable monomer, obtained via oxidation of 5-hydroxymethylfurfural (HMF), a platform chemical derived from lignocellulosic biomass [21, 22]. The resulting furan-based AEI was incorporated into the cathode catalyst layer and benchmarked against the established PPO-LC ionomer. Importantly, the integration of this sustainable ionomer with hydrochar-derived carbon catalyst into the electrode formulation represents an initial step toward a fully biomass-based, environmentally responsible AEMFC components.

2 Experimental

2.1 Materials

2,5-Furandicarboxylic acid (FDCA), thionyl chloride (SOCl₂), p-phenylenediamine, anhydrous dimethylformamide (DMF), dichloromethane (DCM), tetrahydrofuran (THF), lithium aluminium hydride (LiAlH₄), sodium hydroxide (NaOH), and all other chemicals were purchased from Merck and used as received. Carbon paper (AvCarb EP55) and Pt/C 40% cloth gas diffusion

electrodes (0.5 mg/cm²) were obtained from the Fuel Cell Store. Pine needles (PN) were collected from a urban area near the University of Perugia.

2.2 Synthesis

2.2.1 Synthesis of furan-based polyamide

FDCA (0.25 g, 1.6 mmol) and an excess of SOCl₂ were added to a three-neck round-bottom flask equipped with mechanical stirring and under nitrogen atmosphere. The mixture was stirred at 80 °C for 3 hours to convert the diacid into the corresponding acid chloride. After this period, anhydrous N,N-dimethylformamide (DMF, 0.25 mL) was added as a catalyst [23] and the mixture was stirred for an additional 2 hours. The reaction mixture was then cooled to room temperature and the excess SOCl₂ was removed under reduced pressure. In a separate flask, equipped similarly with mechanical stirring and under nitrogen atmosphere, p-phenylenediamine (0.173 g, 1.6 mmol) was dissolved in 10 mL of dichloromethane (DCM) at room temperature. Once completely dissolved, triethylamine (0.89 mL, 6.4 mmol) was added to act as a base. The previously synthesized FDCA chloride was added dropwise to the diamine solution under continuous stirring. The reaction mixture was stirred at room temperature for 48 hours. The resulting polyamide was precipitated in deionized water, filtered, washed thoroughly with water, and dried under vacuum at 80 °C to afford the furan-based polyamide.

2.2.2 Reduction of furan-based polyamide

The dried furan-based polyamide (0.14 g, 0.6 meq) was dissolved in tetrahydrofuran (THF) and stirred at room temperature until a clear solution was obtained. In a separate flask, a solution of lithium aluminium hydride (LiAlH₄) (0.23 g, 6 mmol) in 20 mL of THF was prepared. The LiAlH₄ solution was added slowly to the polyamide solution. The reaction mixture was stirred at room temperature for 48 hours. After completion, the mixture was carefully quenched with 10 mL of deionized water, followed by 40 mL of additional water and 10 mL of 15% NaOH to deactivate any remaining LiAlH₄ and precipitate the reduced polymer. The product was then filtered, washed with deionized water, and dried under vacuum, yielding the reduced furanic polyamine, which was subsequently quaternized for use as an anion exchange ionomer.

2.2.3 Quaternization of poly(N-furfuryl-p-phenylenediamine) (PFPA)

N-methylation of the reduced furan-based polyamide was carried out using CH₃I as the methylating agent. In a three-neck round-bottom flask equipped with mechanical stirring and maintained under a nitrogen atmosphere, 0.14 g (0.7 mmol, 2.8 meq) of the reduced polyamide was

added to 5 mL of anhydrous tetrahydrofuran (THF). The mixture was stirred and heated to 60 °C to ensure complete dissolution of the polymer. Once the polymer was fully dissolved, 0.26 mL (4.2 mmol) of CH₃I was added to the reaction mixture. The reaction was maintained at 60 °C for 24 hours under continuous stirring to allow complete methylation of the amine groups. After completion, the resulting polymer was filtered, thoroughly washed with deionized water, and dried under high vacuum at 80 °C to remove residual solvent and excess methyl iodide. The resulting poly(N-furfuryl-p-phenylenediammonium), named PFPA in the following had an ion exchange capacity (IEC) of 4.09 meq/g.

2.2.4 Synthesis of PPO-LC

The AEM synthesis initiated with the metalation of PPO using n-BuLi for 3 hours at 55 °C [24]. The solution was then cooled to -70 °C and 1,4-dibromobutane was added. After this addition, the reaction mixture was stirred overnight at room temperature. The product was then precipitated in ethanol, filtered, washed with ethanol, and dried. The polymer was dissolved in dimethyl sulfoxide (DMSO) and an excess of TMA (in a 2:1 ratio with respect to the degree of functionalization) was added. The resulting ionomer, PPO-LC, had a degree of amination of 0.38 and an IEC of 0.99 meq/g.

2.2.5 Hydrothermal carbonization of pre-treated PN (sample code: 230_1)

The synthesis of N-containing hydrochars was carried out following the procedure described in Ref. [10]. PN waste was used as feedstock. The pre-treatment involved drying the raw material at 110 °C for 24 hours, followed by solvent extraction using a toluene-methanol azeotrope under reflux for 8 hours. The extracted biomass was subsequently dried under vacuum at 80 °C before use.

For the synthesis, 2.0 g of the pre-treated PN was dispersed in 20 mL of deionized water. The suspension was supplemented with 0.025 g sodium dodecyl sulfate (SDS) as a surfactant and 1.8 g of urea as a nitrogen source. After stirring at 60 °C, the mixture was transferred to an autoclave for hydrothermal treatment. The hydrothermal carbonization was conducted at 230 °C for 1 hour. Following the reaction, the formed hydrochar was separated by filtration and the solid product was dried at 105 °C for 24 hours. The resulting powder was stored in an airtight container for subsequent characterization and electrochemical testing. The 230_1 treatment was selected for this study as it provided the best electrochemical performance among the tested conditions [10].

2.2.6 Hydrothermal carbonization of untreated PN (sample code: 230_1 W)

The PN were mechanically processed by grinding and sieving to obtain a fine powder. Then, 2 g of this powdered PN was mixed with 1.8 g of urea and 20 mL of deionized water. The mixture was homogenized and transferred into a Teflon-lined stainless-steel reactor, which was heated at 230 °C for 1 hour. After cooling to room temperature, the solid product was filtered and washed with hot deionized water to remove residual compounds. The hydrochar was then dried under vacuum at 105 °C until constant weight was reached and stored in a sealed container for further analysis.

2.2.7 Hydrothermal carbonization of untreated PN post-treated (PT) via high-temperature thermal activation (sample code: 230_1 PT)

- (a) Hydrochar was synthesized by mixing 2 g of untreated PN waste with 20 mL of deionized water to maintain a solid-to-liquid ratio of 1:10. The mixture was transferred to a Teflon-lined stainless steel autoclave reactor and heated at 230 °C for 1 hour, using a heating rate of 5–10 °C/min. After cooling to room temperature, the hydrochar was filtered and washed with hot deionized water until the filtrate was colorless, indicating removal of soluble residues. The solid was then dried under vacuum at 105 °C until constant weight was achieved.
- (b) For the post-treatment, the dried hydrochar was mixed with an equal weight of nitrogen-doping agent (melamine) and thermally treated at 800 °C for 1 hour under an inert atmosphere. The resulting post-treated hydrochar was stored in an airtight container prior to further characterization.

2.3 Preparation of catalyst ink and electrode fabrication

The catalyst ink was prepared by dispersing 22.4 mg of hydrochar, 5.6 mg of ionomer (20 wt% PFPA or PPO), and 280 µL of dimethyl sulfoxide (DMSO) in a vial. The mixture was stirred continuously until a homogeneous dispersion was achieved. Subsequently, the dispersion was subjected to ultrasonication to ensure thorough mixing and prevent agglomeration of the catalyst particles. The resulting ink was then drop-cast onto activated carbon paper [25] using a micropipette to control the loading. The coated substrate was dried under high vacuum at 40 °C to remove the solvent and ensure firm adhesion of the catalyst layer to the support [26]. Electrodes were fabricated with various catalyst loadings and were stored in ambient conditions. The composition of the different electrodes is reported in Table 1.

Table 1 Composition of the electrodes

Electrode code	Hydrochar	Ionomer	Deposited mass/mg
H-PFPA-0.09	230_1	PFPA	0.09
H-PFPA-0.16	230_1	PFPA	0.16
H-PFPA-0.23	230_1	PFPA	0.23
H-PPO-0.25*	230_1	PPO-LC	0.25
HW-PPO-0.33	230_1 W	PPO-LC	0.33
HPT-PPO-0.28	230_1 PT	PPO-LC	0.28
HPT-PPO-0.57	230_1 PT	PPO-LC	0.57

Already reported [10]

H=hydrochar, HPT=post-treated hydrochar, HW=hydrochar without pretreatment of pine needles

2.4 Characterization

2.4.1 Ion exchange capacity

The ion exchange capacity of the ionomer was determined by acid-base titration. After the exchange with OH⁻ ions, the ionomer was washed with deionized water and dried. The samples were weighted and immersed in 0.1 N HCl solution to replace the hydroxide ions with chloride ions. The HCl solution was titrated with 0.1 N NaOH. PFPA and PPO-LC had an IEC of 4.09 and 0.99 meq/g, respectively.

2.4.2 Proximate analysis

Proximate composition in terms of moisture (% U), volatile matter (% VM) and ash (% Ash) contents was obtained according to the standard procedures EN ISO 18134-3 [27], EN 15148 [28], and EN 14775 [29], EN 51719 [30]. Fixed carbon (% FC) was derived from Eq 1:

$$\%FC = 100 - \%U - \%VM - \%Ash \quad (1)$$

2.4.3 Elemental analysis

Elemental composition (% C, % H, % N and % S) was determined using a UNICUBE[®] instrument. Oxygen content was estimated by difference according to Eq 2:

$$\%O = 100 - (\%C + \%H + \%N + \%S) \quad (2)$$

The obtained data for the employed hydrochar are presented in Table 2.

2.4.4 Bulk density of hydrochars

To measure the hydrochar bulk density, European Biochar Certificate [31] (VDLUFA-Method A 13.2.1 [32])

protocol was applied. A volume of at least 300 mL of moisture free sample was poured into a graduated cylinder and compressed at least ten times through falling. After that, both mass and volume of the hydrochar were recorded and the final bulk density was calculated. Bulk density values are presented in Table 2 for each hydrochar.

2.4.5 Spectroscopic analysis

¹H NMR was performed with a Bruker Avance 700 spectrometer operating at 700.18 MHz, using deuterated solvent (DMSO-d₆). The Fourier Transform Infrared Spectroscopy (FTIR) spectra were obtained using a Perkin Elmer Spectrum 2 IR spectrometer equipped with an ATR ZnSi crystal. Raman spectra were registered using an Optosky ATR 8300 Micro Raman spectrometer with an excitation wavelength of 785 nm and a laser power of 45 mW.

2.4.6 Optical microscopy

The samples were observed using a Leitz Aristomet microscope and images were captured with an Euromex CMEX-5 camera.

2.4.7 Electrochemical measurements

All electrochemical measurements were performed with a Biologic potentiostat VMP3 equipped with a standard three-electrode system. A platinum foil (4 cm²) served as the counter electrode, the reference electrode was saturated Ag/AgCl/KCl (E=0.197 V vs SHE), and a rotating disk electrode (RDE, OrigaTrod, OrigaLys) was the working electrode. The catalytic electrodes made by drop-depositing each catalyst ink on carbon paper were fixed to a pre-polished glassy carbon disk (3 mm radius). All linear sweep voltammetric measurements for ORR were performed at room temperature in a potential range of 0 to -0.8 V vs Ag/AgCl at a scan rate of 5 mV/s in 0.1 M KOH after a 40 minute oxygen purge. The rotating speed of the RDE was varied between 500 and 2500 rpm. The capacitance measurements were performed by cyclic voltammetry at scan rates between 20 and 100 mV/s in N₂-saturated 0.1 M KOH. The impedance spectra were measured at the open-circuit potential with an a.c. amplitude of 20 mV in a frequency range between 1 Hz and 1 MHz.

Table 2 Elemental composition, ash content, and density of the samples

Sample	C(%)	N(%)	H(%)	O(%) ^a	Ash (%)	Density (kg/m ³)
230_1	45.7	2.5	5.3	39.5	7.0	136
230_1 W	49.5	2.0	4.0	40.0	4.5	260
230_1 PT	75.2	10.5	1.0	4.1	9.2	310

^aCalculated by difference: %O = 100% - %C - %H - %N - %Ash (sulfur content is negligible)

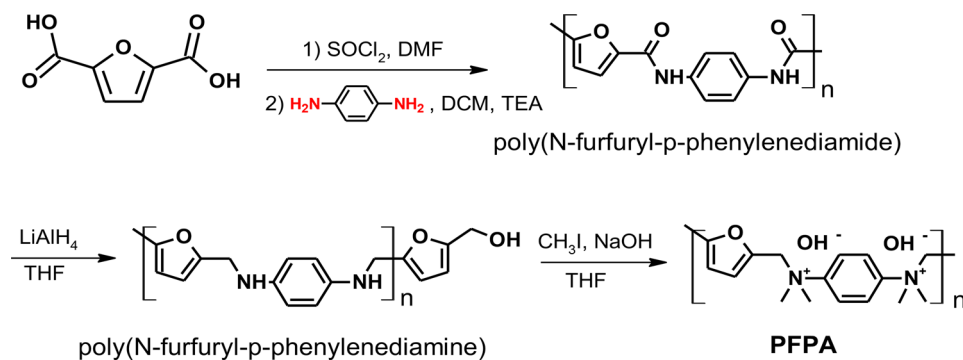


Fig. 1 Synthesis route for the furan-based polymer

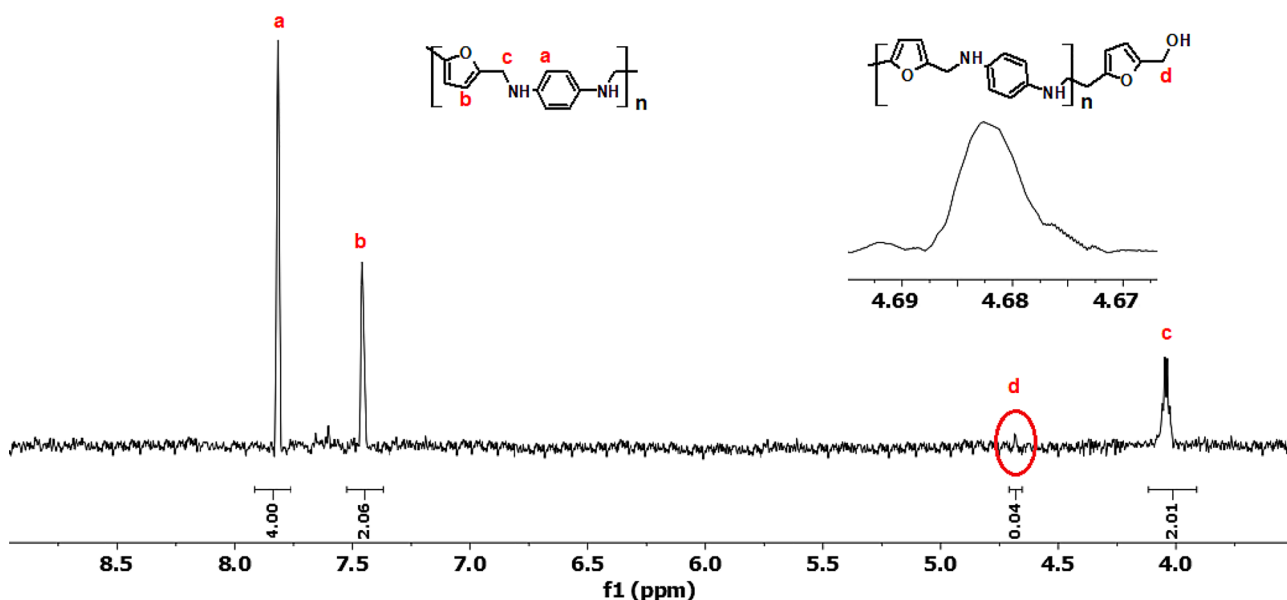


Fig. 2 ^1H NMR spectrum for poly(N-furfuryl-p-phenylenediamine) in $\text{DMSO}-d_6$

3 Results and discussion

3.1 Furan-based ionomer

The anion exchange ionomer PFPA was synthesized following the pathway illustrated in Fig. 1. The process began with the polycondensation of 2,5-furandicarboxylic acid chloride (FDCA-Cl) with p-phenylenediamine, yielding an aromatic furan-based polyamide [33]. To improve the chemical stability of the polymer under alkaline conditions, a reduction step was introduced prior to quaternization. This reduction serves two purposes: it converts the amide moieties into amines, which are more resistant to nucleophilic attack and degradation in high-pH environments typically encountered in AEMFC operation and it facilitates the subsequent quaternization reaction, as the reduced polymer does not contain amide groups that engage the nitrogen electron pair by resonance impeding the functionalization with quaternary ammonium groups. An additional benefit of the reduction step is that it enables a clear identification by NMR of the terminal groups in the polymer chain. Specifically,

the reduction of FDCA-chloride end-groups leads to the formation of furfuryl alcohol, a compound that presents distinctive signals in the ^1H NMR spectrum (Fig. 2). After reduction, the polymer was quaternized using an alkylating agent to introduce fixed cationic sites along the polymer chain, imparting hydroxide ion conductivity necessary for ionomer function in the catalyst layer.

The structure of the synthesized poly(N-furfuryl-p-phenylenediamine) was confirmed by ^1H NMR spectroscopy [22], as shown in Fig. 2. Figure S1 reports the ^1H NMR spectrum of the corresponding amide (poly(N-furfuryl-p-phenylenediamide)). The spectrum in Fig. 2 displays three main regions of interest: signal (a) corresponds to the aromatic protons of the p-phenylenediamine moiety; signal (b) is assigned to the furan ring protons, originating from the furanic backbone; signal (c) appears in the aliphatic region and is attributed to the methylene protons ($-\text{CH}_2-\text{NH}-$) adjacent to the amine group, generated after the reduction. An expansion of the aliphatic region of the spectrum highlights

a distinct signal at 4.68 ppm, which is attributed to the methylene group of furfuryl alcohol, a chain termination product formed through reduction of the FDCA-derived monomer end groups [34]. This signal serves as a diagnostic marker confirming the presence of furfuryl alcohol at the polymer chain ends. An alternative termination route could involve unreacted p-phenylenediamine end groups, which would be expected to give rise to a peak at approximately 6.7–6.5 ppm [35]. However, this signal is absent in the spectrum, indicating that chain termination preferentially (and perhaps exclusively) occurs through the furan-based monomer rather than the diamine. One method to determine the number-average molecular weight (M_n) of a polymer is the end-group analysis [36]. Here, the integration of the furfuryl alcohol peak (d) relative to the aromatic peaks provides an estimate of the degree of polymerization. The integration ratio corresponds to 0.04H relative to 2H (furfuryl alcohol methylene), which suggests the presence of approximately 50 repeat units per polymer chain. Considering a repeat unit mass of 200 g/mol, a degree of polymerization of 50, and an end-group mass of 97 g/mol, the number-average molecular weight (M_n) of poly(N-furfuryl-p-phenylenediamine) is estimated to be 10100 g/mol. The poly(N-furfuryl-p-phenylenediammonium) (PFPA) is not soluble in any classical solvent. The FTIR of the quaternized polymer is reported in the SI (Figure S2).

3.2 Hydrochars

Three hydrochars were synthesized as described in the Experimental section, using both pre-treated and untreated biomass along with different thermal treatments to investigate how these variables affect the material's elemental composition and physical properties. While samples 230_1 and 230_1 W were synthesized using urea as the nitrogen source to explore nitrogen doping during hydrothermal carbonization,

the post-treatment step for sample 230_1 PT employed melamine as the doping agent. This choice was made because melamine, with its higher nitrogen content and thermal stability, is more effective at introducing nitrogen functionalities and enhancing the structural ordering of hydrochar during the high-temperature treatment [37]. Thus, the variation in nitrogen precursors reflects an optimization strategy to tailor the hydrochar properties according to the targeted application.

The synthesized hydrochar samples exhibit clear variations in their elemental composition (Table 2). Sample 230_1 shows moderate carbon content (45.7%) and relatively high oxygen content (39.5%, calculated by difference according to equation 2). The nitrogen content is relatively low (2.5%), consistent with the use of urea as additive during the synthesis. Hydrogen is present at 5.3%, typical of hydrochar produced under mild hydrothermal conditions. The ash amounts to 7.0%, and the density is relatively low at 136 kg/m³, reflecting the high bulk porosity of the hydrochar.

Sample 230_1 W corresponds to hydrochar synthesized via hydrothermal carbonization with urea as a nitrogen source, but without any pre-treatment of the biomass. Compared to 230_1, this sample shows increased carbon content (49.5%) and a notable reduction in hydrogen (4.0%) and ash (4.5%). The nitrogen content slightly decreases to 2.0%, while the oxygen content remains similar (40.0%). The density nearly doubles to 260 kg/m³, indicating a more compact structure (see below).

Finally, sample 230_1 PT exhibits a substantial increase in carbon, and nitrogen content to 75.2% and 10.5%, respectively. Hydrogen drops sharply to 1.0%, indicating a more condensed carbon structure with fewer volatile groups. The oxygen content is drastically reduced to 4.1%, consistent with partial graphitization and deoxygenation. The ash slightly increases to 9.2%, possibly due to thermal concentration effects. The density further increases to 310 kg/m³, reflecting a denser and more graphitic material.

The Raman spectra of the three hydrochar samples are reported in Fig. 3, focusing on the region between 1300 and 1600 cm⁻¹. This region includes two characteristic bands: the D-band and the G-band, commonly used to characterize carbon materials. The D-band is typically associated with structural defects or disordered carbon, while the G-band corresponds to graphitic or sp²-hybridized carbon domains. The heterogeneous composition of chars complicates the full interpretation of their Raman spectra, although some considerations can be made. As shown in Fig. 3, the wavenumber of the D-band decreases (1360 cm⁻¹ for 230_1 PT vs 1390–1400 cm⁻¹ for 230_1 and 230_1 W) and that of the G-band slightly increases (1540 cm⁻¹ with a shoulder at 1560 cm⁻¹ for 230_1 PT vs 1520 cm⁻¹ for 230_1 W) for the sample obtained at

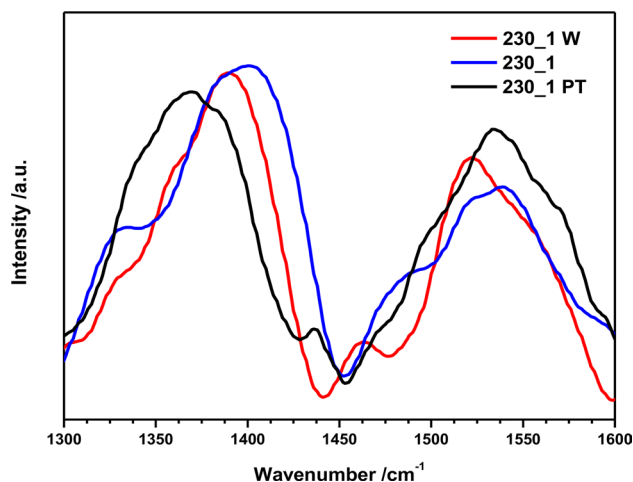


Fig. 3 Raman spectra of the different hydrochars

higher temperatures. This shift is generally interpreted as an increase in the structural order of the carbon material. The observed changes suggest that as the treatment temperature rises, volatile compounds such as alkanes and C–O-containing groups are released, leading to increased aromatization of the hydrochar structure [38].

It has been reported that for solid carbon materials containing substantial amounts of small polycyclic aromatic hydrocarbons (PAHs) like pyrene or perylene, the spectral region around $1370\text{--}1410\text{ cm}^{-1}$ tends to broaden and increases in intensity. High concentrations of these PAHs result in distinct peaks, whereas low concentrations produce minor shoulders adjacent to the primary D-band, indicating the presence of larger polycyclic clusters, as observed especially for 230_1 PT and 230_1 W samples. Furthermore, the $1480\text{--}1550\text{ cm}^{-1}$ region is attributed to mixed breathing and asymmetric stretch modes of sp^2 carbons near defects, often leading to out-of-plane deformations. Heteroatom doping or defects in this region can also cause redshifts in peak positions. The results suggest significant changes in cluster size, defect density, and chemical composition, indicating an increasing degree of order and a reduction in oxygen content as the treatment temperature increases [39, 40].

The intensity ratio I_D/I_G (1.15, 1.35, 1.65 for 230_1 PT, 230_1 W, 230_1 respectively) decreases with the temperature, suggesting a higher proportion of condensed aromatic ring structures [41]. A comparison between samples 230_1 and 230_1 W shows that 230_1 has a lower content of aromatic ordered structures (see also Table 2). This is likely due to the pre-treatment applied to 230_1, which removes aliphatic molecules from the pine needles, resulting in lower carbon content in the feedstock. Since these aliphatic carbon groups play an

important role in breaking down and forming aromatic compounds during the hydrothermal carbonization process, their removal reduces the formation of aromatic structures. Therefore, skipping the pre-treatment with organic solvents like toluene and methanol not only makes the process more sustainable but also promotes the development of a more aromatic hydrochar structure [42]. A simplified structure of hydrochar is reported in Fig. 4.

3.3 Catalytic electrodes for the ORR

The composition of the electrodes is reported in Table 1. Optical micrographs of H-PFPA-0.09 and HPT-PPO-0.57 (Figure S3) show a homogeneous distribution of inks on the surface of carbon paper.

3.3.1 Electrochemically active surface area (ECSA)

Potentiostatic Electrochemical Impedance Spectroscopy was performed on all samples. Impedance spectra of the hydrochar/PFPA and hydrochar/PPO electrodes are shown in Fig. 5a and b.

All impedance spectra were analysed using the z-fit software by defining an equivalent circuit containing resistances (R) and constant phase elements (CPE) Q in a series (-) and parallel (//) configuration. The impedance of a CPE can be written:

$$Z(CPE) = \frac{1}{Q} (j\omega)^{-n} \quad (3)$$

j is the imaginary unit and ω the angular frequency. Q is the CPE value and n the CPE exponent, characteristic of the physical nature of the element: values near 1 indicate an imperfect capacitance and near 0.5 a Warburg-type diffusion-limitation.

The circuit R1 - R2//Q2 - Q3 contained R1 attributed to electrolyte and electrode resistance, R2 to the charge transfer resistance and Q2 to the interfacial capacitance. Q3 had comparable values to the capacitance measured by the cyclic voltammetric method.

The non-linear least-square fit parameters are shown in Table 3. The electrode resistance (R1) values are slightly lower for HPT and HW containing electrodes, probably related to the higher conductivity of these biochars due to the larger content of ordered aromatic structures (see the discussion of Raman spectra above). The low charge transfer resistances (R2) indicate good electrocatalytic activity; the higher R2 value for H-PFPA-0.23 does however not correspond to a significantly lower performance. The very high Q2 values and corresponding n_2 around 0.6 indicate mass-transport limitations (Warburg-type impedance). The systematically higher values of Q3 for the hydrochar/PPO samples are consistent with the values obtained by cyclic voltammetry. They show a higher

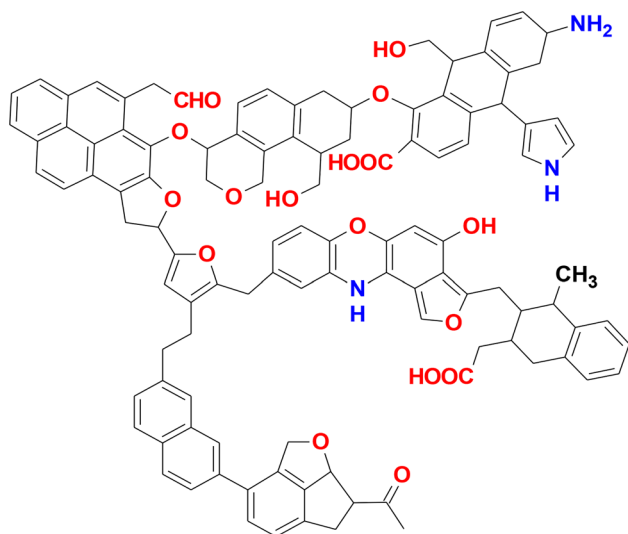


Fig. 4 Simplified representation of hydrochar structure with relevant functional groups

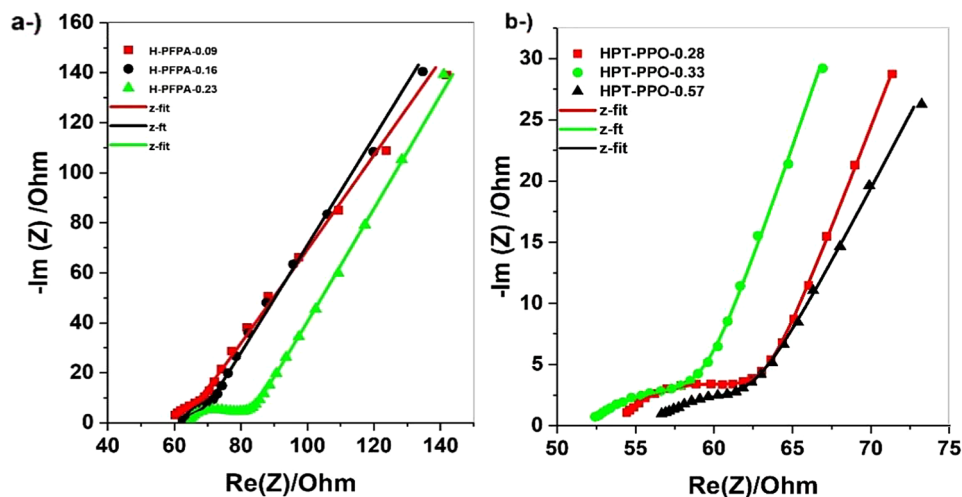


Fig. 5 Impedance spectra in O_2 -saturated 0.1 M KOH of **a)** hydrochar/PFPA and **b)** hydrochar/PPO-LC electrodes (symbols: experiment, lines: zfit plot)

Table 3 Summary of PEIS analysis of various biochar-based electrodes and comparison with Pt/C benchmark. *c* is the electrode capacitance determined by cyclic voltammetry

Samples	Pt/C	H-PFPA-0.09	H-PFPA-0.16	H-PFPA-0.23	HPT-PPO-0.28	HPT-PPO-0.57	HW-PPO-0.33
R1/ Ω	60.7	56.6	62.7	62.7	53	52	56
R2/ Ω	2.2	7.1	4.5	19.8	9.2	7.1	6.5
Q2/ $\mu F.s^{(a-1)}$	4702	642	273	97	723	1975	1978
a2	0.6	0.6	0.8	0.6	0.7	0.6	0.6
Q3/ $mF.s^{(a-1)}$	5.9	1.7	1.6	1.7	7.4	8.9	7.2
a3	0.7	0.6	0.7	0.7	0.8	0.8	0.7
C/mF	-	1.2	1.0	1.5	2.8	6.4	3.9

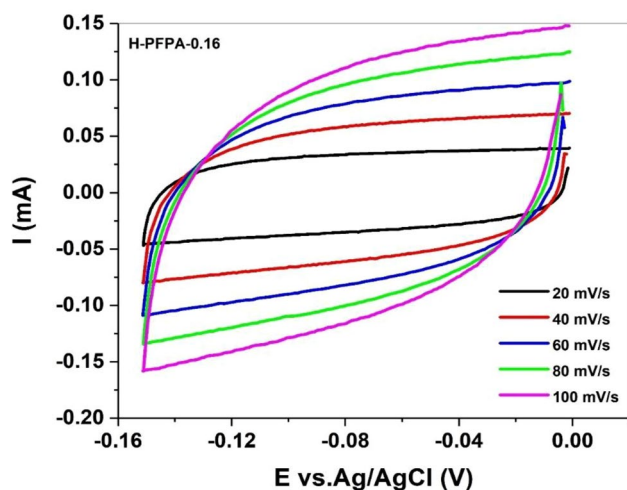


Fig. 6 Cyclic voltammograms for capacitance analysis of H-PFPA-0.16

electrochemically active surface area (ECSA) indicating a better accessibility of catalytic centres.

A typical electrode capacitance measurement by cyclic voltammetry at scan rates between 20 and 100 mV/s in the potential range between 0 and -0.16 V vs. Ag/AgCl, where no Faradaic reactions occur, is shown in Fig. 6. The expected approximately rectangular shape of the curves can be observed. Cyclic voltammograms for the other

electrodes are reported in the Supporting information (Figure S4).

According to Eq. 4, the capacitance C is determined from the non-Faradaic current I at various scan rates.

$$I = C \cdot \frac{dU}{dt} \quad (4)$$

The average capacitance values C are reported in Table 3; the consistency of the values for positive and negative polarization is good.

The capacitances of biochar/PFPA electrodes are much lower than that biochar/PPO electrodes, which show very high electrochemically active surface areas, in accordance with the findings by EIS.

3.3.2 Linear sweep voltammetry (LSV) of ORR

The LSV for hydrochar/PFPA samples (Fig. 7) were conducted at different rotation rates (500, 1000, 1500, 2000, and 2500 rpm) to observe the impact of electrode rotation on the electrochemical behaviour.

The LSV curves exhibit the typical “S-shaped” profile for the ORR. Three regions can be identified: a kinetic region at >0.7 V vs RHE, a mixed control region (0.7–0.5 V vs RHE), and a diffusion-controlled plateau between

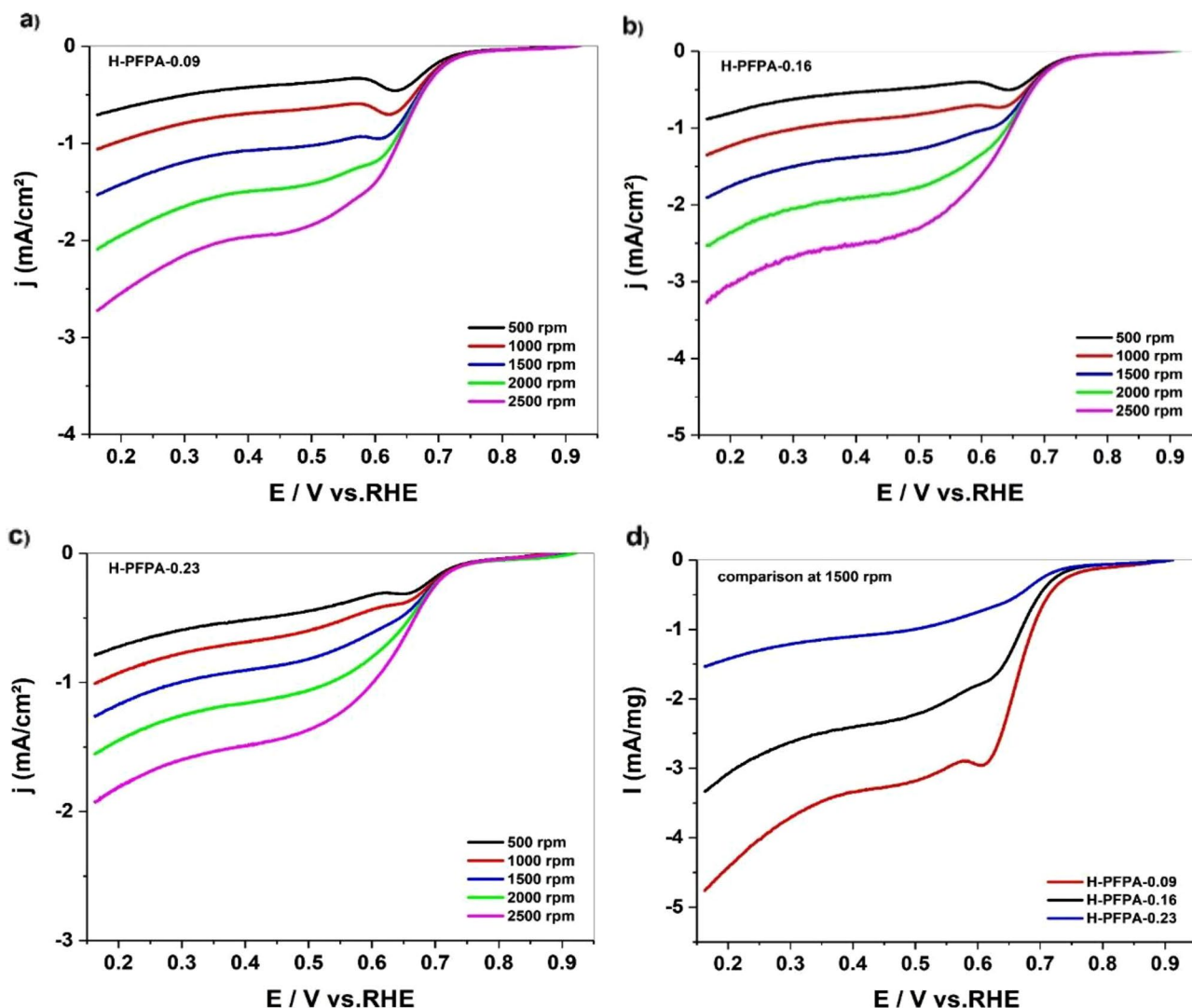


Fig. 7 Linear sweep voltammograms in O_2 -saturated 0.1 M KOH of hydrochar/PFPA electrodes with different mass loading **a)** 0.09 mg, **b)** 0.16 mg, **c)** 0.23 mg at rotation rates of 500 to 2500 rpm. **d)** comparison of mass-specific currents at 1500 rpm

0.5–0.3 V vs RHE. The current density during ORR is related to the rotation speed of the electrode, confirming the mass transport-dominated behaviour below 0.5 V vs RHE.

The highest mass-specific catalytic activity is observed for the biochar electrodes containing the lowest mass of 0.09 mg, as demonstrated in the comparative plot of Fig. 7d. The better electrocatalytic performance of lower mass electrodes is likely due to an increased availability of catalytic sites that allows more reactants to interact with the catalyst, improving the efficiency of the ORR. Similar results have been reported for Pt electrodes, where thin-film electrodes showed much higher electrocatalytic activity than bulk samples [43]. The electrodes with higher catalyst content (0.16 mg, 0.23 mg) have a lower activity, likely due to the more difficult oxygen transport to reach the active sites.

LSV for hydrochar/PPO samples (Fig. 8) show higher current densities than samples containing PFPA. Another advantage of these electrodes is the better electronic transport in hydrochars with a higher content of aromatic structures. The ionomer is crucial for the hydroxide ion transport near the catalyst particles; a poor ionomer dispersion can lead to a less effective catalyst layer, hindering the overall electrochemical performance because the formed hydroxide ions are not transported away from the electrode.

A comparison of three catalyst loadings at a fixed rotation speed (1500 rpm) shows that the hydrochar electrode with the lowest mass (0.28 mg) exhibited again the highest mass-specific catalytic activity for ORR, consistent with the previous explanation.

Figure 8b shows that the HW-PPO electrode provides a current of 3.5 mA/mg at 2500 rpm, demonstrating that

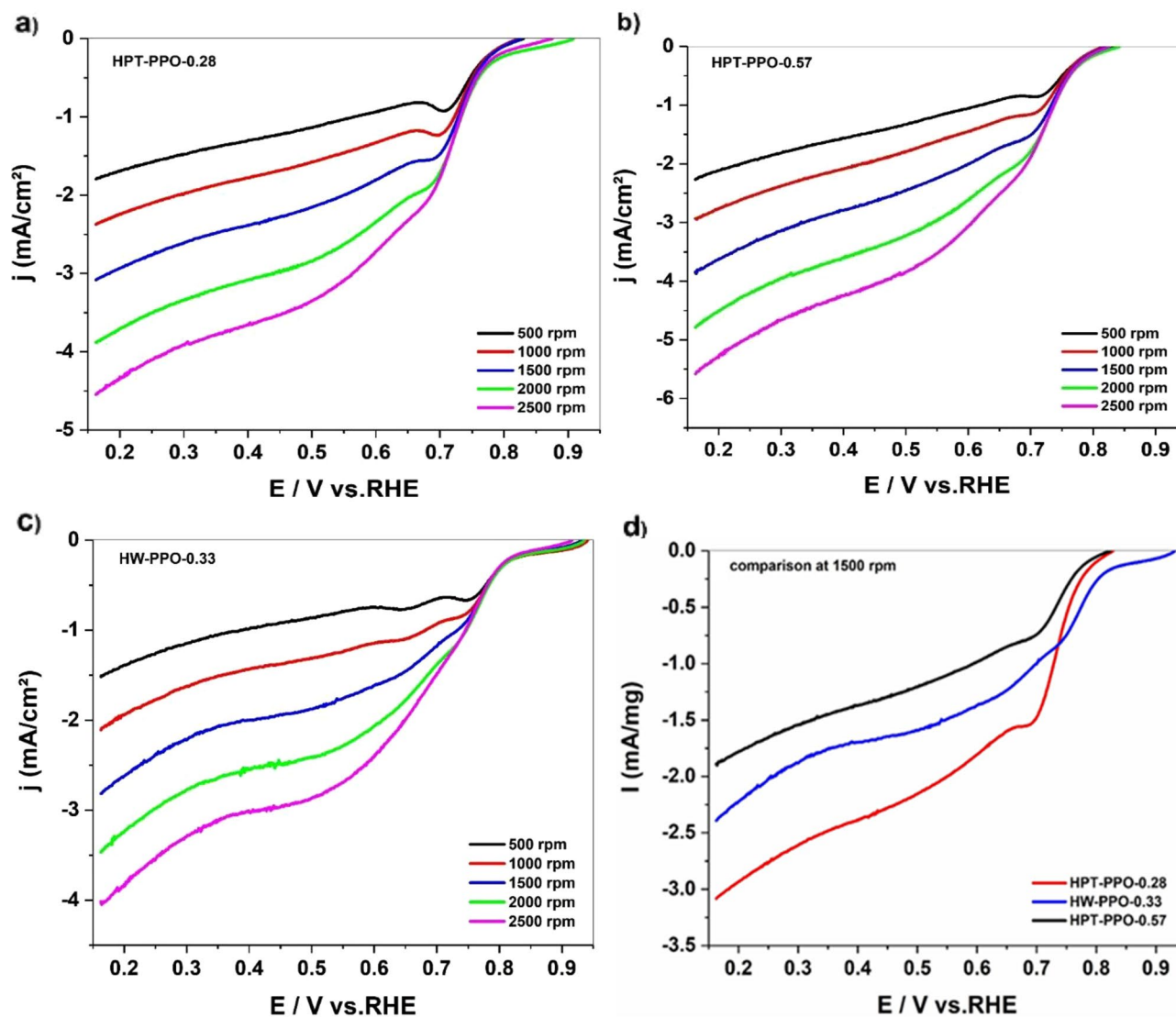


Fig. 8 Linear sweep voltammograms of hydrochar/PPO electrodes in O_2 -saturated 0.1 M KOH at 500 to 2500 rpm with various catalyst masses: **a)** 0.28, **b)** 0.57, and **c)** 0.33 mg. **d)** Mass-specific currents at 1500 rpm

hydrochar can perform effectively in ORR even without solvent-intensive pre-treatment.

3.3.3 Koutecky Levich and Tafel plots

The number of transferred electrons per molecule of reduced O_2 during the ORR can be calculated by the Koutecky-Levich theory using Eq. (5):

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L} \quad (5)$$

Here, j is the measured current density, j_k the kinetic current density, related to charge transfer only, and j_L the limiting current density, described by the Levich equation:

$$j_L = 0.62 \cdot n \cdot F \cdot c \cdot D^{2/3} \cdot \nu^{-1/6} \cdot \omega^{1/2} \quad (6)$$

ω is the rotating disk electrode rate (rad/s), n the number of exchanged electrons, F Faraday's constant (96485 C/mol), C the oxygen saturation concentration in 0.1 M KOH (1.26×10^{-6} mol/cm³), D the oxygen diffusion coefficient in 0.1 M KOH (1.98×10^{-5} cm²/s), and ν the kinematic viscosity of 0.1 M KOH (0.01 cm²/s). n can be calculated by plotting the inverse of the limiting current density ($1/j_L$) against the square root of the rotation rate ($\omega^{1/2}$). Examples of calculation are shown in the SI (Figure S5).

Important electrocatalytic properties, including the number of exchanged electrons, the onset and the half-wave potentials are reported in Table 4. The number of

Table 4 Number of exchanged electrons, onset potentials, half wave potentials, and electrode masses before and after the experiments

Sample	Number of electrons (n)	Onset Potential E_{onset} /V vs RHE	Half-wave Potential $E_{1/2}$ /V vs RHE	Mass before ORR/mg	Mass after ORR/mg
Pt/C 40%	4	0.93	0.87	4.9	4.8
H-PFPA-0.09	1	0.90	0.67	2.6	2.6
H-PFPA-0.16	1.1	0.89	0.67	3.2	3.2
H-PFPA-0.23	1	0.91	0.68	2.7	2.5
HPT-PPO-0.28	2	0.92	0.73	2.8	2.8
HPT-PPO-0.57	2.5	0.84	0.72	-	-
HW-PPO-0.33	1.7	0.93	0.76	2.8	2.7

electrons calculated for Pt/C 40% is 4 and for hydrochar electrodes between 1 to 2.5.

As evidenced in Table 4, the electrodes containing biomass-based PFPA show lower electrochemical performance, especially a lower number of exchanged electrons, compared to previous results with similar hydrochars but containing poly(phenylene oxide) with long side chains (PPO-LC) ($n=3.2$) [10]. Whereas the onset potentials of all electrodes are quite similar and comparable to the Pt/C benchmark, the half-wave potentials are clearly superior for the electrodes containing PPO-LC, attributable to the more efficient hydroxide ion transport. However, it is important to note that the furanic ionomer presents significant potential for sustainability improvement. Previous experiments suggest that introducing long aliphatic chains into the furan backbone could enhance its performance by improving polymer flexibility, increasing ionic conductivity, and optimizing the interaction with the catalyst layer [20].

The mass of electrodes does not change during ORR, showing that no dissolution of electrode components happened during use.

Regarding hydrochar processing, the additional thermal post-treatment applied to the hydrochar, aimed at improving graphitization and electronic conductivity, and the higher nitrogen content did not result in significant performance gains in comparison with the previously published data [10]. Furthermore, this post-treatment is energy-intensive, and from a sustainability standpoint, it is not justified given the marginal benefits. This highlights the importance of balancing performance improvements with the energy and environmental costs associated with materials processing. Interestingly, the hydrochar obtained from non-pretreated pine needles, preserving the native biomass composition, also showed good performance, especially considering its minimal processing requirements. This approach eliminates the need for organic solvents, making it the most sustainable option among those tested. Despite the slightly lower performance compared to pre-treated samples, the simplicity and reduced environmental impact of this

method position it as a promising candidate for further optimization.

3.3.4 Conclusion

In this study, we explored the integration of a biomass-derived ionomer with hydrochar-based electrocatalysts as an initial step toward the development of a fully biomass-based and environmentally responsible anion exchange membrane fuel cell (AEMFC). The furan-based ionomer was synthesized, characterized, and employed as both an anion exchange ionomer and a binder. The performances were compared with an ionomer containing long side chains (PPO-LC).

We also investigated hydrochars derived from pine needles, using different processing strategies to assess their effects on the resulting material properties and electrochemical performance. Electrochemical testing revealed that electrodes incorporating the biomass-based furan ionomer exhibited lower performance, particularly a reduced number of exchanged electrons, as determined by Koutecky–Levich analysis. Linear sweep voltammograms showed onset potentials similar across all electrodes and comparable to the Pt/C benchmark. However, the half-wave potentials were significantly higher in electrodes containing PPO-LC, likely due to enhanced hydroxide ion transport in that system.

Potential improvements to the polymer structure were identified. Specifically, the introduction of long aliphatic chains into the furan backbone could enhance the ionomer's performance by improving polymer flexibility, increasing ionic conductivity, and optimizing its interaction with the catalyst layer.

Regarding hydrochar processing, the additional thermal post-treatment, intended to enhance graphitization and nitrogen content, did not result in substantial performance gains. Furthermore, the energy-intensive nature of this step makes it unsustainable, particularly given the limited benefits. This highlights the need to balance performance enhancements with the energy and environmental costs associated with materials processing.

Interestingly, hydrochar derived from non-pretreated pine needles showed promising performance despite its

minimal processing. This finding suggests that simplified processing routes can be sufficient to produce effective biomass-derived electrocatalytic materials, reinforcing the alignment with sustainability objectives.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1007/s44308-025-00009-8>.

Supplementary Material 1

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Author contributions

S. C., R. N. and E.S. synthesized and characterized the ionomer and prepared the electrodes. A.M. and E. C. synthesized and characterized the hydrochar. A.H. and L.P. performed the electrochemical measurements. P.K. and M.L.D.V. supervised the work and wrote the main manuscript text. All authors reviewed the manuscript.

Data availability

No datasets were generated or analysed during the current study.

Declarations

Competing interests

The authors declare no competing interests.

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