

N-doped Activated Carbon-Supported Cu-Fe-Zn-Ni-Co High-Entropy Alloy Electrocatalyst: Improved ORR in Microbial Fuel Cells

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Abstract

Microbial fuel cells (MFCs) enable simultaneous wastewater treatment and energy recovery; however, their performance is primarily limited by sluggish oxygen reduction reaction (ORR) kinetics at the cathode. In this work, a non-precious metal-based electrocatalyst i.e., Cu-Fe-Zn-Ni-Co (CFZNC) high-entropy alloy (HEA) supported on nitrogen (N)-doped activated carbon powder (ACP) was synthesized and evaluated for ORR activity. CFZNC-HEA/N-ACP exhibited excellent ORR performance with E_{onset} and $E_{1/2}$ of 1.12 V and 0.82 V vs RHE, respectively, and high selectivity towards a four-electron ORR pathway, indicating direct reduction of O_2 to H_2O . It delivered the highest open-circuit potential (0.85 V), outperforming CFZNC (0.62 V) and N-ACP (0.21 V) alone as an MFC cathode. The superior performance is attributed to synergistic multi-metal active sites in HEA nanoparticles and N-doped porous carbon support, which enhance ORR kinetics and reduce cathodic overpotential. These results highlight the potential of noble metals-free cost-effective HEA-based cathodes for advancing MFC electrocatalysis.

Introduction

The ever-growing global demand for clean and sustainable energy, coupled with the detrimental environmental effects of fossil fuel combustion, has intensified the pursuit of green energy technologies. Among emerging alternatives, microbial fuel cells (MFCs) stand out as a promising platform that offers a compelling route for coupling wastewater remediation with electricity production [1]. In MFCs, exoelectrogenic microbes catalyze the conversion of biodegradable organic matter into bioelectricity through their metabolic processes [2, 3]. Briefly, organic pollutants are oxidized in the anode chamber of an MFC via microbial catalytic activity of exoelectrogenic bacteria in biofilm formed over the anode under anaerobic conditions, generating hydrogen ions (H^+) and electrons (e^-). H^+ and e^- are transported through proton exchange membrane (PEM) and external electrical pathway, respectively, where they arrive at the cathode chamber. In the cathode chamber, oxygen reduction reaction (ORR) utilizes e^- , followed by the combination with H^+ to produce water. A critical determinant of the overall MFC performance is the cathodic ORR, a kinetically sluggish, multi-electron transfer process that significantly impacts the energy conversion efficiency of the electrochemical device [4, 5].

Traditionally, platinum-based catalysts have been employed to enhance ORR owing to their high activity. However, owing to limitations related to expense, availability, and poisoning resistance that impede commercialization [6, 7]. This has spurred intensive research into cost-effective and efficient alternative materials. In this context, the composites of cost-effective and earth-abundant transition metals including Cu, Fe, Ni, Co, and Zn; and porous carbon, doped with N heteroatom, have been explored as electrocatalysts for ORR activity [8–12]. These composite catalysts have remarkably performed for ORR in aqueous electrolyte media because of the catalytic activity of the metals and N-doped carbon, where N-doping in the carbon matrix changes the material's local charge density and electronic distribution because of the electronegativity difference between C and N [13]. This helps to enhance oxygen (O_2) adsorption, lessens the reaction energy barrier and boosts the capability for ORR using metals.

The integration of multiple transition metals into a single-phase solid solution, known as high-entropy alloys (HEAs), represents a paradigm shift in electrocatalyst design [14–16]. Unlike traditional binary or ternary alloys, HEAs are composed of five or more elements having compositions (atomic %) ranging between 5 and 35. HEAs also have configurational entropy change ($\Delta S_{\text{conf}} \geq 1.5R$, where R is the universal gas constant [17]. HEAs exhibit high configurational entropy, lattice distortion, and synergistic electronic interactions among constituent metals, leading to tuneable adsorption energies and enhanced catalytic activity [18, 19]. Recent studies have utilized the Cu, Fe, Ni, Co, and Zn (CFZNC) transition metals with the other metals (Pt, Au, Pd, V, Zr, etc) in HEAs for exploring their ORR activity [20–26]. Mechanistically, the atoms of the transition metals i.e., Fe, Co, and Ni at the HEA surface showed less positive d-band center values than the corresponding monometallic nanoparticles (NPs), resulting in an enhanced ORR performance.

The present study reports the synthesis of N-doped activated carbon supported non-precious metal-based HEA NPs comprising of Cu, Fe, Zn, Ni, and Co, (CFZNC-HEA/N-ACP). The synthesis of CFZNC-HEA/N-ACP involves polymerization of phenol and formaldehyde with simultaneous in situ metal precursor impregnation, followed by grinding of the metal-polymeric composite and subsequent thermal treatments, including carbonization, steam-activation, and hydrogen-reduction. The ORR electrocatalytic performance of CFZNC-HEA/N-ACP is systematically evaluated by analysing electrochemically active surface area (ECSA), and current density, onset potential (E_{onset}), and half wave potential ($E_{1/2}$), and compared with those of the CFZNC metal mixture and N-ACP. Furthermore, the practical applicability of the synthesized catalyst is demonstrated in a working MFC, using open circuit potential (OCP) measurements and cyclic operational stability tests.

Materials and methods

List of reagents

All reagents were utilized as supplied, without additional purification in this study. Solutions were prepared using ultrapure (Milli-Q) water. Comprehensive information on the reagents utilized in this study is provided in the Supporting Information (SI).

CFZNC-HEA/N-ACP synthesis

The procedure to synthesize CFZNC-HEA/N-ACP was similar to the protocol as that outlined in earlier studies, with necessary refinements [15, 16]. Briefly, the synthesis method constituted four steps i.e., synthesis of metal precursor impregnated polymeric beads; ball milling; thermal treatment including carbonization cum calcination, steam activation and H_2 -reduction; and the nitrogen impregnation. Fig. S1 shows a detailed block diagram of CFZNC-HEA/N-ACP synthesis. Metal precursor-loaded beads were synthesized by polymerizing the phenol and formaldehyde co-polymers in a polymerization reactor made of glass. The polymerization essential reagents such as monomers (phenol and formaldehyde), catalyst

(triethylamine), suspension stabilizing agent (poly vinyl-alcohol), crosslinking agent (hexamethylene tetraamine) and CFZNC metals precursor solutions were sequentially added in polymerization reactor to preform suspension polymerization. After completion of the reaction, the CFZNC metals-impregnated polymeric beads were separated from polymeric suspension using sieves and kept overnight for drying at room temperature (RT ~ 25°C).

The CFZNC metal salt impregnated polymeric beads were first pulverized in ball mill (Retsch, Germany), resulting in a fine metal salt-loaded polymeric powder. This powder was then carbonized and steam activated. The obtained porous activated material was subsequently reduced under a hydrogen atmosphere. The final product was designated as CFZNC-HEA/ACP for further reference. The N-doping required the impregnation of the produced CFZNC-HEA/ACP with the aqueous solution of urea (1 g urea in 10 ml water) for 1 h, where urea was used as nitrogen source and water was evaporated [27]. The resultant powdery material was annealed at 900°C in O₂-free environment i.e. N₂ for 1 h in the electric furnace. The produced material was termed CFZNC-HEA/N-ACP. N-ACP (N-doped activated carbon) and CFZNC metal mixture were separately synthesized as reference materials for the comparative ORR performance. The N-ACP sample was synthesized following the same protocol used for CFZNC-HEA/N-ACP, with omitting the use of metal salts. For CFZNC metal mixture, the mixed metal salt solution was first dried and then calcined directly, without incorporating any carbon support.

Methods for characterization and electrochemical measurements

The synthesized materials were thoroughly characterized by means of advanced analytical techniques such as scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), N₂ adsorption-desorption isotherms, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and inductively-coupled plasma mass-spectrometry (ICP-MS).

For electrochemical evaluation, glassy carbon electrode (GCE) was used as substrate to prepare working electrodes and analyses were performed using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and linear sweep voltammetry (LSV) coupled with rotating-disc electrode (RDE). Detailed procedures for material characterization and electrode preparation are provided in the SI.

MFC set-up, operation, and measurements

A H-type MFC was used in the study, having the anode and cathode chamber, separated by the Nafion 117 PEM. Cathodes were fabricated on pretreated activated carbon fabric (ACF) support by the spray coating of catalyst ink. E. coli LB broth (~ 10¹⁰ CFU/ mL) was used for the inoculation of MFC and glucose-based substrate (500 mg/L COD) served as the substrate for microbial activity. The MFCs were operated in batch mode. All experiments were performed three times to check the repeatability. Detailed descriptions of the MFC configuration, operation and measurements are provided in the SI.

Results and discussion

Morphological, compositional and structural characteristics

The morphological and compositional characteristics of the synthesized electrocatalysts were comprehensively examined using the SEM, TEM, and EDS techniques to evaluate their potential as the cathodic ORR catalysts for MFC. The SEM images of the synthesized CFZNC-HEA/N-ACP are shown in Fig. 1 (a-b). The low-magnification SEM image reveals a highly porous and textured carbon framework decorated with uniformly dispersed HEA NPs, which is further confirmed by SEM-EDS elemental mapping. This morphological feature of CFZNC-HEA/N-ACP is highly desirable for the cathode of MFCs, as it facilitates effective O_2 diffusion and enhances the availability of reaction sites at the interface of O_2 gas, electrolyte, and catalyst. The high-magnification SEM image of CFZNC-HEA/N-ACP further reveals homogeneously distributed quasi-spherical NPs embedded within the porous matrix, forming continuous conductive pathways that are expected to enhance electron transport and lower charge-transfer resistance during the ORR. On the other hand, N-ACP was observed to have porous web-like structure, while CFZNC exhibited smooth nonporous smooth surface (Fig. S2).

The compositional characteristics of the electrocatalyst were analysed by means of SEM-EDS elemental mapping. The elemental composition confirms the successful incorporation of CFZNC metals along with substantial carbon and nitrogen content (Fig. 1c). Elemental mapping further demonstrates the homogeneous spatial distribution of CFZNC

metals and N across the carbon matrix, validating the formation of a multi-metallic HEA supported on N-doped carbon (Fig. 1d-i). The HEA formation is further confirmed by AAS analysis. Notably, the uniform nitrogen distribution is particularly beneficial for ORR, as N-doped carbon enhances electrical conductivity and facilitates faster electron transfer kinetics at the cathode, thereby contributing to an improved MFC performance.

TEM imaging was further performed to examine the nanoscale morphological and structural features of the synthesized CFZNC-HEA/N-ACP. The TEM micrograph reveals that HEA NPs were anchored on the carbon support, indicating effective metal-support interaction (Fig. 1j). The TEM micrograph of CFZNC-HEA/N-ACP was used to analyse size distribution of particles on N-ACP support. and the results is shown in Fig. 1k. The results revealed that the HEA NPs had sizes ranging from 10 to 70 nm, with an average diameter of 30.25 nm, which is favourable for maximizing the exposure of active sites. The high-resolution TEM exhibits well-defined lattice fringes with an interplanar spacing of approximately 0.25 nm, confirming the crystalline characteristics of the alloy phase (Fig. 1l). This interplanar spacing is indexed to the (0 0 2) crystallographic plane of CFZNC-HEA/N-ACP, which is consistent with XRD results. The absence of distinct lattice planes corresponding to individual metals further supports the formation of a single-phase HEA structure. Such a structure is expected to enhance ORR catalytic activity due to lattice distortion and sluggish diffusion effects inherent to HEAs, which can optimize the adsorption energies of O_2 intermediates.

ICP-MS was further conducted to find out the bulk elemental composition of the synthesized materials. The elemental composition of CFZNC-HEA/N-ACP, along with the calculated configurational entropy (ΔS_{conf}) values for each constituent element is summarized in Table 1. The molar compositions of all metallic elements were found to be in the range of 12.41–26.65%, which satisfies the compositional criterion for HEA formation (5–35%). In addition, the calculated ΔS_{conf} value of 1.58R exceeds the typical threshold value (1.5R) required to classify a material as a HEA, confirming the successful formation of the HEA phase in CFZNC-HEA/N-ACP. On the other hand, the measured molar composition (2.35–41.42%) and calculated ΔS_{conf} value (1.26R) for CFZNC did not meet the HEA formation criteria, indicating the absence of HEA formation (Table S1). These results highlight the crucial role of the carbon support in CFZNC-HEA/N-ACP, which helps prevent elemental segregation during high-temperature processing steps of calcination, activation, and reduction [16, 28]. The absence of such stabilization in CFZNC likely led to phase separation, thereby hindering HEA formation.

The structural evolution of the synthesized materials was carried out using XRD patterns. Figure 2a shows the XRD patterns of the synthesized CFZNC-HEA/N-ACP, CFZNC, and N-ACP. N-ACP exhibited two broad diffraction peaks at around 24.91 and 43.97°, corresponding to the (0 0 2) and (1 1 1) planes of carbon, attributed to partially graphitized carbon structure [29, 30]. On the other hand, CFZNC displayed sharp and intense reflections at 43.43, 50.63, and 74.29° indexed to the (1 1 1), (2 0 0), and (2 2 0) planes, indicating the formation of metallic phases arising from the aggregation of individual metals [31–33]. For CFZNC-HEA/N-ACP, the diffraction pattern is dominated by a broad carbon (0 0 2) peak accompanied by weak and slightly shifted metallic reflections. Compared to CFZNC, the metallic peaks of CFZNC-HEA/N-ACP exhibit noticeable peak broadening and slight shifts in the 2θ positions, which is attributed to lattice distortion induced by the incorporation of multiple metal elements with different atomic radii into a single solid-solution lattice. Such lattice distortion is a characteristic feature of HEA which can modify the electronic structure of the material and optimize the adsorption energies of O_2 intermediates, thereby enhancing ORR kinetics.

Table 1
Elemental composition (mole%) measuring
by ICP-MS and $\Delta S_{\text{conf.}}$ of the synthesized
CFZNC-HEA/N-ACP.

Metals	Composition (Mol. %)	$\Delta S_{\text{conf.}}$
Cu	26.65	0.35
Fe	24.64	0.35
Zn	12.41	0.26
Ni	17.65	0.31
Co	18.66	0.31
Total		1.58

The graphitic characteristics of the synthesized samples were examined by Raman spectroscopy, and the corresponding spectra are provided in Fig. 2b. Both CFZNC-HEA/N-ACP and N-ACP exhibit two prominent bands at approximately 1330 and 1600 cm^{-1} , which are associated with disordered sp^3 carbon (D-band) and well-ordered sp^2 -hybridized graphitic carbon (G-band), respectively [34]. The presence of the degree of graphitisation is beneficial for electrocatalysis, as they facilitate transportation of electrons and facilitate consistent distribution of active sites, thereby enhancing ORR performance. Notably, the ratio of D band intensity (I_D) to G band intensity (I_G) decreases from 0.93 in N-ACP to 0.91 in CFZNC-HEA/N-ACP, showing improved graphitization in the HEA-supported catalyst. The improved graphitization is because of the metal NPs, which promote the transformation of polymeric carbon into more ordered graphitic structure during high-temperature treatment; ultimately it is expected to improve electrical conductivity which supports the ORR kinetics [35].

The specific surface area (S_{BET}) and porous characteristics of synthesized materials were examined by N_2 -adsorption/desorption isotherms based on the BET method. The isotherms (Fig. 2c) and corresponding textural parameters (Table 2) demonstrate significant differences in the porosity and surface area of the materials. N-ACP exhibited a high adsorption of N_2 gas at $P/P_0 < 0.1$, a characteristic of the microporous structure, which is reflected in its high S_{BET} ($1112 \text{ m}^2 \text{ g}^{-1}$) and dominant micropore-volume (V_{Micro} , 0.58 cc g^{-1}). In comparison, CFZNC-HEA/N-ACP shows a gradual adsorption increase across the entire P/P_0 range, indicating the presence of both microporous and mesoporous domains. This hierarchical pore architecture is further supported by its nearly equal micropore (0.42 cc g^{-1}) and mesopore (0.25 cc g^{-1}) volume contributions, along with the high S_{BET} of $736 \text{ m}^2 \text{ g}^{-1}$. Such porous architecture is highly favorable for electrocatalytic ORR, as micropores provide abundant active sites, while mesopores facilitate rapid O_2 diffusion and electrolyte transport, thereby minimizing mass transfer limitations in MFC cathodes [36]. On the other hand, CFZNC exhibited a low S_{BET} ($38 \text{ m}^2 \text{ g}^{-1}$) with

negligible microporosity, with its pore volume dominated by mesopores (0.06 cc g^{-1}), which limits active site exposure and is expected to result in inferior ORR performance.

Table 2
 S_{BET} and pore volume distribution of synthesized materials.

Material	S_{BET} (m^2/g)	V_{Total} (cc/g)	V_{Micro} (cc/g)	V_{Meso} (cc/g)
CFZNC-HEA/N-ACP	736	0.67	0.42	0.25
N-ACP	1112	0.62	0.58	0.04
CFZNC	38	0.07	0.01	0.06

The surface elemental composition and valence states of the CFZNC-HEA/N-ACP catalyst were investigated using XPS analysis. The survey spectrum confirms the coexistence of all constituent elements, including CFZNC metals and N demonstrating the successful integration of the five-metal of the HEA formulation onto the N-doped ACP support (Fig. 2d). The high-resolution Cu 2p spectrum displays two primary peaks at 932.3 eV and 952.1 eV, attributed to the Cu 2p_{3/2} and Cu 2p_{1/2} states of metallic Cu⁰, respectively (Fig. 2e) [37]. Similarly, the Fe 2p spectrum shows a dominant peak at 706.8 eV, assigned to metallic Fe⁰ (Fig. 2f) [38]. For Zn 2p, the peaks at 1021.1 eV and 1044.3 eV are attributed to the Zn⁰ state (Fig. 2g) [16]. The Ni 2p spectrum reveals Ni⁰ peaks at 852.0 eV and 858.2 eV (Fig. 3h) [39]. Furthermore, the Co 2p spectrum exhibits two major peaks at 778.1 and 783.0 eV for metallic Co⁰ (Fig. 2i) [40]. The predominance of zero-valent metallic states across all the five transition metals confirms the successful reduction and formation of the HEA phase. The carbon framework was analyzed using the C 1s spectrum, which was deconvoluted into three distinct components: graphitic sp² C (285.8 eV), sp³ C (285.3 eV), and carbonyl groups (C = O) at 288.6 eV (Fig. 2j) [41]. This indicates a highly graphitic structure with functional O₂ groups that facilitate catalyst dispersion. The N 1s spectrum further confirms the successful N-doping. The spectrum is deconvoluted into two major peaks: pyridinic-N at 400.9 eV and graphitic-N at 397.6 eV (Fig. 2k) [42]. The pyridinic and graphitic-N content are known to

significantly enhance ORR activity by providing active sites for O₂ adsorption that facilitate electron transfer through coordination with the neighbouring active sites and improve the electrical conductivity of the N-doped support [42]. Therefore, this synergistic coupling of the HEA particles and the N-doped porous C architecture is expected to improve the cathodic performance CFZNC-HEA/N-ACP in MFC.

Electrochemical study

Firstly, the electrocatalytic activity of the synthesized CFZNC-HEA/N-ACP towards ORR was evaluated using CV measurements in the Ar- and O₂-saturated aqueous 0.1 M KOH electrolyte solution (Fig. 3a). CFZNC-HEA/N-ACP demonstrated O₂ reduction peak in Ar-saturated electrolyte solutions. The results

indicate that CFZNC-HEA/N-ACP is stable in the electrochemical working window. Conversely, CFZNC-HEA/N-ACP exhibited a distinct cathodic peak centered at 0.66 V, indicating electrochemical response to the presence of O₂ in the electrolyte solution and pronounced electrocatalytic activity towards ORR. The ORR electrocatalytic activity was also compared with the other synthesised materials i.e., CFZNC and N-ACP by performing CVs in electrolyte solution with O₂ saturation (Fig. 3b). An electrocatalytic activity towards O₂ was also observed for CFZNC and N-ACP. Compared to CFZNC and N-ACP, CFZNC-HEA/N-ACP achieved highest intensity of O₂ reduction peak, indicating a greater number of active sites and better ORR performance. The E_{onset}, (at 0.1 mA/cm²) reflects how readily the ORR proceeds on the catalyst surface [43]. The positive E_{onset} of CFZNC-HEA/N-ACP (1.12 V) compared to CFZNC (0.96 V) and N-ACP (0.98 V) indicated the ORR easily taking place at the catalyst surface, and therefore, CFZNC-HEA/N-ACP has better catalytic activity towards ORR. This enhanced performance arises from improved electron transfer, lowered activation barriers, and faster reaction kinetics that is because of the synergetic effect of HEAs and N-doped activated carbon.

ECSA and charge-transfer resistance (R_{ct}) were evaluated to assess electrocatalytic characteristic of the synthesized samples. CVs at different scan rates were performed in K₃Fe(CN)₆ solution in PBS for ECSA (Fig. 3c and S3 (a, a')). Randles-Ševčík (RS) equation (equation – 1) was used to determine ECSA [44]:

$$i_p = 0.4463nACF\left(\frac{nFvD}{RT}\right)^{0.5}$$

1

where, i_p is peak current, n is number of electrons transferred, A is ECSA, C is the concentration of K₃Fe(CN)₆ solution, D is the diffusion coefficient, F is Faraday's constant, v is scan rate, and T is the solution temperature (K). Figure 3d and S3 (b, b') shows the plots of peak current vs square root of scan rate, which were used to determine the ECSA. The calculated ECSAs were normalized to GCE area (geometrical). The synthesized CFZNC-HEA/N-ACP, CFZNC, and N-ACP exhibited ECSAs of 6.242, 2.31, and 1.19 cm².cm⁻², respectively. The substantially superior electrochemical area of CFZNC-HEA/N-ACP shows a greater electroactive site, which contributes to superior electrocatalytic performance.

The interfacial properties of the electrocatalysts were analysed using EIS performed at OCP. The Fig. 3e shows the Nyquist plots drawn using EIS data. The solution resistance (R_s), R_{ct} , and Warburg (diffusion) resistance (R_w) parameters were determined by EIS data fitting to an equivalent Randles circuit (Table S2). All EIS measurements were carried out under identical electrolyte compositions (0.1 M KOH) and experimental conditions, as confirmed by the consistent R_s values of approximately 20 Ω observed for all electrodes. CFZNC-HEA/N-ACP demonstrated R_{ct} value of 64 Ω, which is lowest among CFZNC (92 Ω) and N-ACP (209 Ω). These results suggest that CFZNC-HEA/N-ACP offers improved electrical conductivity attributed to strong interaction and synergistic effects between the HEA NPs and graphitic characteristics of ACB, thereby enabling more efficient charge transport across the catalyst-electrolyte interface [45].

For a deeper understanding of the O₂-reduction kinetics, ORR kinetic parameters of the CFZNC-HEA/N-ACP were calculated from LSVs measured using RDE setup. The RDE experiments were conducted in O₂-saturated 0.1 M KOH aqueous solution at the scan rate of 10 mV s⁻¹ at different rotation rate (ω) of 400–2000 rpm, as illustrated in Fig. 4a. An increase in the maximum current density was observed with increasing ω , which enhances O₂ transport

through the electrolyte and thereby improves the catalytic activity. These observations indicate that ORR at the surface of CFZNC-HEA/N-ACP was diffusion-controlled [7, 34]. The ORR current limited by mass transport was observed near ~ 0.7 V. The Koutecky-Levich (K-L) plot was constructed from the RDE data of CFZNC-HEA/N-ACP as shown in Fig. 4b. The K-L plot shows the variation of current density with ω . All data fitted lines in the K-L plot have approximately the same slopes (B), confirming ORR occurring at the surface of CFZNC-HEA/N-ACP exhibits first-order dependence on the concentration of dissolved O₂ [46]. The average charge transfer number (n) was calculated using K-L equation (equation-2 and 3).

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{B\omega^{0.5}}$$

2

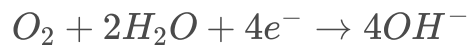
where, Levich slope (B) is expressed as follows.

$$B = 0.62nFC_{O_2}D_{O_2}^{2/3}\nu^{-1/6}$$

3

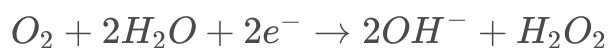
where, J represents current density (mA/cm²), F represents the Faraday-constant (96,485 C mol⁻¹), C_{O₂} represents the oxygen concentration (1.22 × 10⁻⁶ mol cm⁻³), D_{O₂} (1.9 × 10⁻⁵ cm² s⁻¹) represents the O₂ diffusion coefficient in 0.1 M KOH, and ν is the kinematic viscosity of the electrolyte (0.0113 cm²s⁻¹). ORR typically proceeds via either a 4e⁻ pathway, reducing O₂ directly to H₂O, or a 2e⁻ electron pathway, forming H₂O₂ as an intermediate. For MFC applications, the 4e⁻ route is preferred due to its higher efficiency and selectivity [34]. The 4e⁻ and 2e⁻ ORR pathways are given below [47]:

4e⁻ ORR pathway

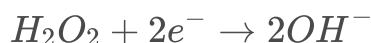


2

2e⁻ ORR pathways



3



4

The value of n was found to be 4.1 which is close to the theoretical value of 4, indicating that ORR proceeds predominantly via $4e^-$ pathway mechanism [47]. ORR through the $4e^-$ pathway mechanism at the CFZNC-HEA/N-ACP surface also confirms that hydrogen peroxide (H_2O_2) was not formed as an intermediate and O_2 was completely reduced to water. The high value of n reflects an excellent ORR activity and indicates that the HEA NPs enhance O_2 adsorption and activation.

The ORR electrocatalytic performance of the synthesized samples was also analysed by performing RDE experiment at selected ω (1600 rpm) ensuring sufficient O_2 mass transport, resulting in a diffusion-limited current and enabling reliable comparison of ORR activity under standardized hydrodynamic conditions (Fig. 4c). CFZNC-HEA/N-ACP exhibited higher diffusion limiting current density (8.64 mA/cm^2) at 0.7 V compared to CFZNC (6.12 mA/cm^2) and N-ACP (2.16 mA/cm^2). Furthermore, CFZNC-HEA/N-ACP exhibited $E_{1/2}$ of 0.82 V whereas at CFZNC exhibited 0.79 V. The enhanced electrocatalytic activity towards ORR is attributed to the synergistic interaction of metal atoms and N-doped activated carbon.

Performance of materials as the cathode in MFCs

The cathodic electrochemical performance for the power generation of the prepared CFZNC-HEA/N-ACP, CFZNC, and N-ACP was further evaluated in the MFC constructed using these materials i.e., CFZNC-HEA/N-ACP, CFZNC, and N-ACP. Initially, MFCs were operated under batch and OCP conditions to determine the OCP value which is the theoretical maximum voltage achievable by the system under ideal conditions. Under OCP condition, the system has infinite resistance in the absence of the load connection with no electric current flowing through the circuit. A stable voltage was established in retention time of 2 days, ensuring thorough infusion of the bacterial culture into ACF used as anode in all MFCs. The MFC using the CFZNC-HEA/N-ACP cathode exhibited the highest and fastest-stabilizing OCP (859 mV), followed by CFZNC (622 mV) and N-ACP (208 mV), highlighting the critical role of HEA active sites in the N-ACP substrate enhancing O_2 reduction kinetics and cathode potential (Fig. 4d). This improvement in OCP is expected to translate into reduced polarization losses and enhanced power output under closed-circuit operation.

Figure 4(e-f) show the power density curves and the corresponding polarization curves of the MFCs provided with synthesised cathode materials. Importantly, the maximum power density of cathode materials in MFCs was observed to follow the order as: CFZNC-HEA/N-ACP (0.26 mW cm^{-2}) > CFZNC (0.13 mW cm^{-2}) > N-ACP (0.02 mW cm^{-2}). In addition, the maximum OCP generated by CFZNC-HEA/N-ACP is 0.85 V, followed by CFZNC (0.62V), and N-ACP (0.21 V). Approximately similar OCP results were measured manually using multi-meter which are shown in Fig. 4c. The MFC using CFZNC-HEA/N-ACP also achieved highest maximum current density 1.32 mA/cm^2 followed by CFZNC (0.87 mA/cm^2) and N-

ACP (0.23 mA/cm^2). CFZNC-HEA/N-ACP has shown promising results which are better than or comparable with most of the recently reported electrocatalysts employed for ORR, as presented in Table S3 [27, 36, 46–50]. The performance of CFZNC-HEA/N-ACP catalyst is attributed to the HEA NPs of different metals and the N-doped porous structure of activated carbon support, which could not only alleviate the aggregation of HEA NPs and enhance conductivity, but also provided more effective contact area between O_2 and electrolyte, thus speeding up O_2 transportation to enhance the MFC performance.

Conclusions

An ORR electrocatalyst *viz.* CFZNC-HEA/N-ACP, consisting of the HEA NPs of CFZNC metals and N-doped activated carbon support was developed as an efficient non-precious cathode for MFCs. Structural analyses confirmed the formation of a HEA with uniform elemental dispersion and strong metal-support interaction within a hierarchical porous carbon matrix. Electrochemical studies revealed that the synergistic interaction between HEA NPs and the conductive N-doped carbon support optimized oxygen adsorption and accelerates interfacial electron transfer, resulting in a high onset potential (1.12 V), half-wave potential (0.82 V vs RHE), low charge-transfer resistance, and a dominant four-electron ORR pathway. These mechanistic advantages directly translated into the improved MFC performance, delivering a higher open-circuit voltage (0.85 V) and power density (0.26 mW cm^{-2}) compared to the control cathodes. The results confirm that the electronic interactions and lattice strain effects that are inherent to HEAs and synergistically integrated with tailored carbon supports, constitute an effective design strategy for achieving enhanced durability and catalytic efficiency in the ORR-based bioelectrochemical energy systems.

Declarations

Author contributions

Naveen Kumar Verma: Data curation, Investigation, Methodology, Writing original draft, Validation, Formal analysis. Basker Sundararaju: Investigation, Conceptualization, Formal analysis, Writing – review & editing, Supervision. Nishith Verma: Conceptualization, Project administration, Formal analysis, Resources, Funding acquisition, Supervision, Writing – review & editing.

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Data availability

Data will be made available on request from the authors.

Statements and declarations

Competing interests- All the authors declare no competing interests.

Ethical approval- Not applicable

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Figures

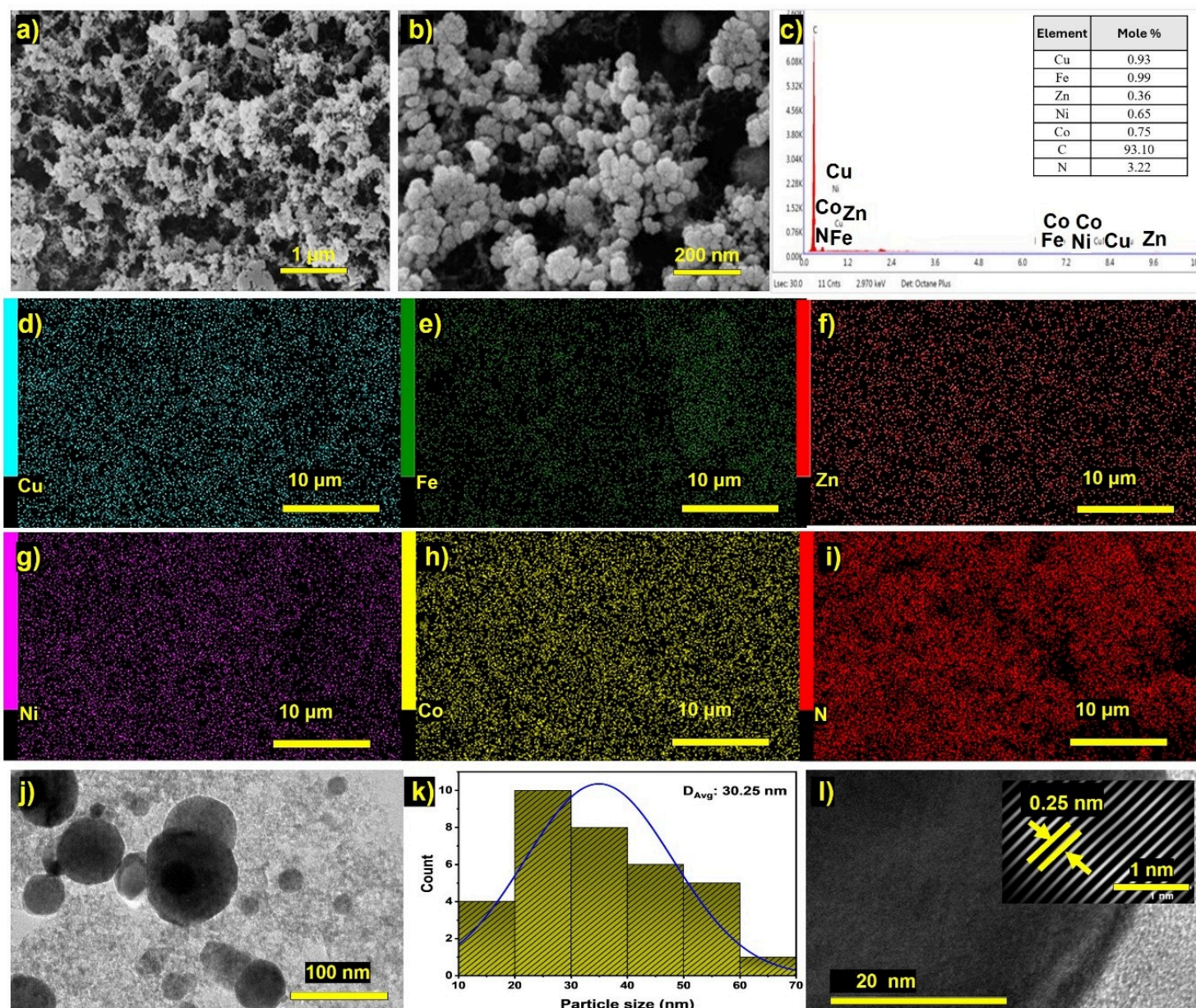


Figure 1

(a and b) low and high magnification SEM images of CFZNC-HEA/N-ACP, (c) EDS spectra of CFZNC-HEA/N-ACP, (d-i) elemental mapping of CFZNC-HEA/N-ACP, (j) TEM image of CFZNC-HEA/N-ACP, (k) HEA particle size distribution, and (l) HR-TEM image of CFZNC-HEA/N-ACP.

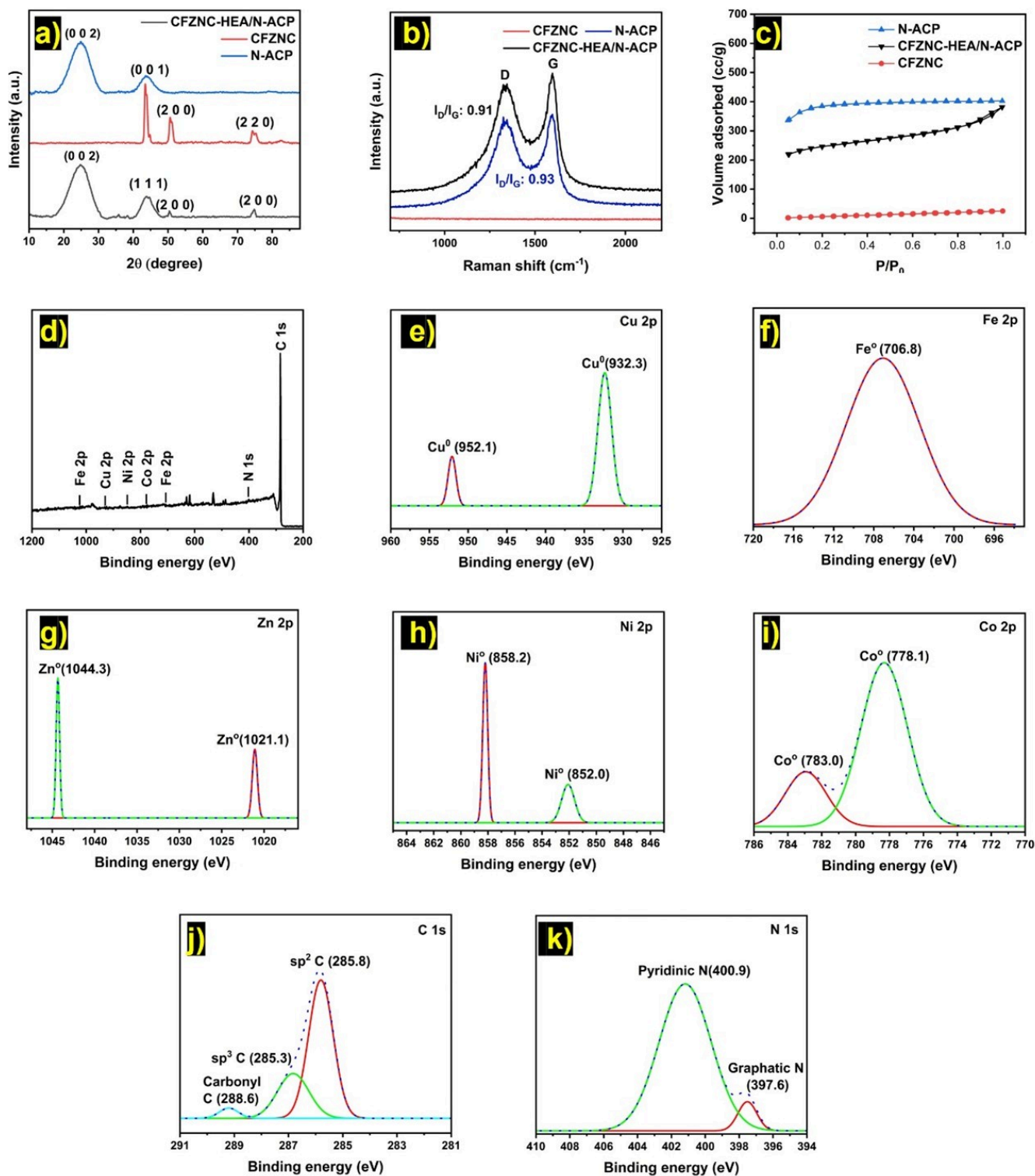


Figure 2

(a) XRD patterns of the synthesized materials, (b) Raman spectra of the synthesized materials, (c) N_2 -adsorption-desorption isotherms of the synthesized materials, and (d-k) XPS spectra of CFZNC-HEA/N-ACP.

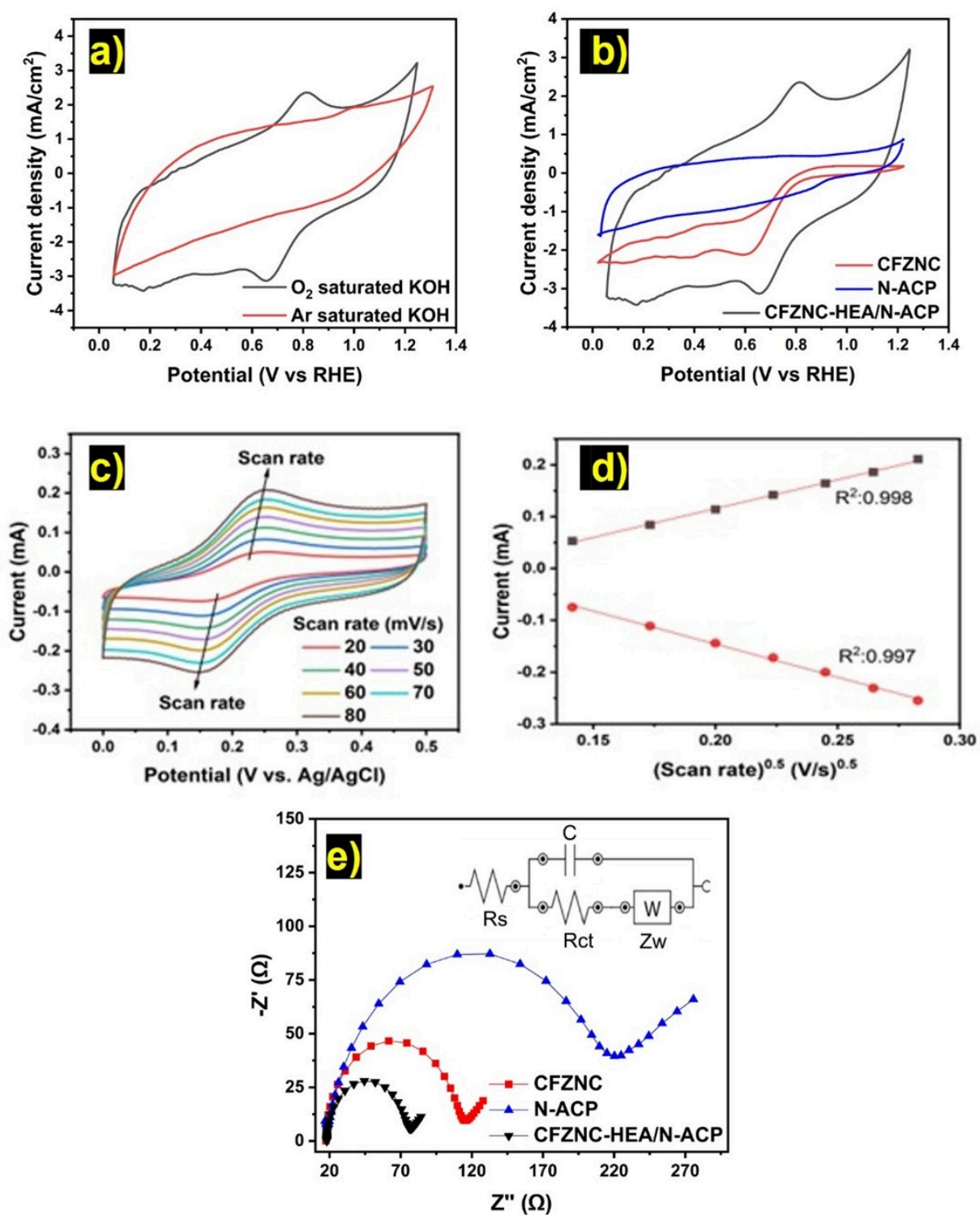


Figure 3

(a) CV spectra for CFZNC-HEA/N-ACP in Ar and O_2 -saturated electrolyte solution, (b) CV spectra for CFZNC-HEA/N-ACP, CFZNC and N-ACP in O_2 -saturated electrolyte solution, (c-d) CVs and data fitting curves for ECSA estimation for CFZNC-HEA/N-ACP, and (e) EIS plot for CFZNC-HEA/N-ACP, CFZNC and N-ACP.

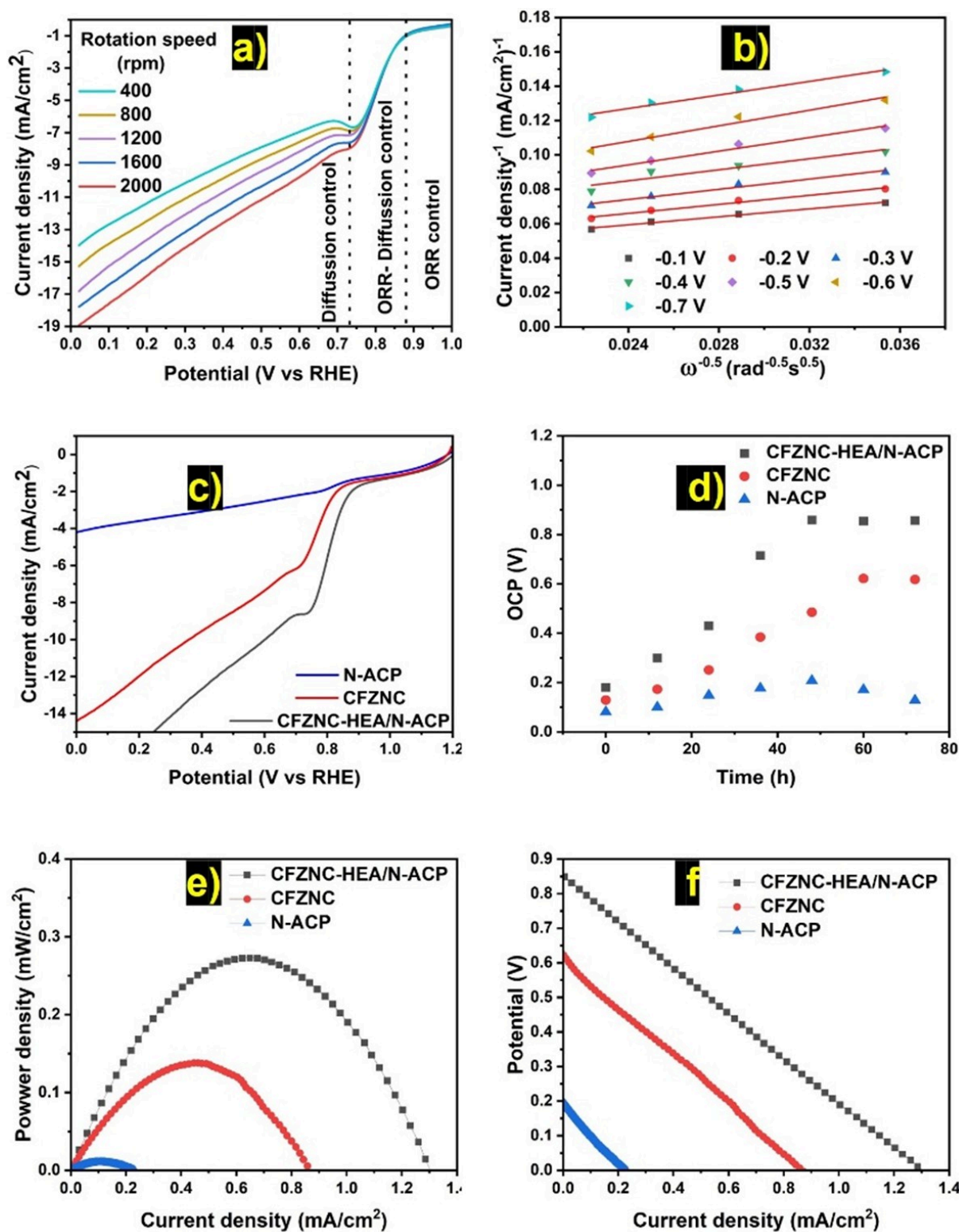


Figure 4

(a-b) RDE LSV-curves (at different rpm) of CFZNC-HEA/N-ACP in O₂-saturated electrolyte solution and corresponding fitting curves, (c) RDE LSV-curves (at 1600 rpm) of

CFZNC-HEA/N-ACP, CFZNC, and N-ACP in O₂-saturated electrolyte solution, (d-f) variation in OCPs with time, the power density curves, and the corresponding polarization curves of the MFCs using the

cathode catalysts, namely, CFZNC-HEA/N-ACP, CFZNC, and N-ACP.

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