

Magnetically-altered e_g -orbital occupancy to boost the two-electron oxygen reduction electrocatalysis for faster water decontamination

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ARTICLE INFO

Keywords:

Electro-Fenton
Ferromagnetic MOF
 H_2O_2 production
Magnetoelectrocatalysis
Oxygen reduction reaction

ABSTRACT

Herein, we demonstrate how the magnetic modulation of the e_g -orbital occupancy of Co ions can become a novel approach to enhance the two-electron oxygen reduction reaction ($2e^-$ ORR) for advanced wastewater treatment by electro-Fenton (EF) process. Nickel foam (NF) substrate coated with ZIF67 was prepared and thermally treated to obtain ferromagnetic NF-supported Co/Co₃O₄ cathodes, whose response to a small magnetic field was further evaluated in EF. The results show an increase of 62.3 % increase in H_2O_2 yield and 46.5 % in faradaic efficiency, improving the degradation rate of the antibiotic sulfamerazine from 77.2 % to 92.4 % in 120 min. This enhancement is attributed to improved electron transfer facilitated by the alteration of e_g -orbital occupancy of Co ions caused by spin regulation under the magnetic field, rather than to mass transport effects. Therefore, magnetic modulation of the e_g -orbital occupancy emerges as a promising strategy to boost EF process for more efficient water decontamination.

1. Introduction

The electro-Fenton (EF) process has gained attention over the last decade as an advanced wastewater treatment technology [1–4]. The electrogeneration of H_2O_2 directly at the cathode via two-electron oxygen reduction ($2e^-$ ORR, Eq. 1) avoids the environmental risks of industrial H_2O_2 synthesis and handling, which are inherent to the conventional Fenton process (Eqs. 2 and 3). The key to improve the EF performance is boosting the H_2O_2 yield through optimization of the electrocatalyst activity/selectivity for the occurrence of Eq. 1 [5,6]. Therefore, significant research emphasis has been put on various approaches to modulate the electronic effects of electrocatalysts in the EF process [7–9].



The promotion of the $2e^-$ ORR electrocatalysis relies on the d-band center theory introduced by Nørskov et al. [10], which links the electrocatalyst adsorption strength for reactants to the inherent activity of key sites and their electronic structures [11,12]. In transition metal complexes, the d electrons closer to ligands have higher energies than those at greater distance, leading to a splitting of the d orbitals into two groups with different energy levels [13,14]: The lower-energy orbitals - d_{xy} , d_{xz} , and d_{yz} - are collectively referred to as t_{2g} , while the higher-energy orbitals - d_{z^2} and $d_{x^2-y^2}$ - are called e_g (Fig. S1 in Supplementary Material file). The unique involvement of d-orbitals in transition metals significantly influences their bonding patterns. σ and π are the two main forms of d-orbital bonding in an octahedral complex: The t_{2g} -orbitals are able to form π -bonds with ligands because their orientation (Fig. S1) allows for the necessary sideways overlap with the ligands' p or π -orbitals; on the other hand, the σ -bonds primarily involve the electrons of the e_g -orbitals of the metal and the ligands' s, p, or hybridized orbitals. Since the e_g -orbitals point directly at the ligands, which impedes the required type of overlap, π -bonding is unsuitable with these electrons. In contrast, δ bonds only exist in materials

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<https://doi.org/10.1016/j.apcatb.2025.125149>

Received 27 November 2024; Received in revised form 6 February 2025; Accepted 9 February 2025

Available online 11 February 2025

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involving transition metals [15] and only involve electrons in e_g -orbitals, which are also those mainly affected by the magnetic field in this study. Since the e_g -orbitals of transition metal ions participate in σ -bonding with surface adsorbates (e.g., O_2) and facilitate charge transfer at the catalytic interface, their occupancy has a significant influence on the binding of intermediates to active sites and on reaction dynamics [16]. Therefore, regulating the number of electrons occupying the e_g -orbitals can modulate the related reactions. Among diverse strategies (like size modulation [17], defect induction [18], lattice substitution [19]) to regulate the number of electrons occupying the e_g -orbitals, the use of magnetic fields has emerged very recently [13,20]. However, to date, research on magnetic field-alteration of the occupancy of the e_g -orbitals to enhance the two-electron ORR in EF processes remains very limited, despite the promising reports of magnetic field-induced changes in e_g -orbital occupancy that allow improving the HER and OER [21–24].

Therefore, in this study, we demonstrate a magnetically-induced modification of e_g -orbital occupancy of Co ions to enhance the $2e^-$ ORR. A magnetized ferromagnetic zeolitic imidazolate framework (ZIF67) cathode was employed for H_2O_2 production and EF application. Unlike the conventional synthesis method using ethanol as a solvent, deionized water was employed to create a novel shuttle-shaped ZIF67 variant. This newly formed ZIF67 exhibited a higher aspect ratio and superior loading capacity as compared to the standard octahedral structure. Electrochemical analysis revealed an enhanced ORR performance with the incorporation of ZIF67 onto nickel foam (NF) substrate, and its performance was further ameliorated by exposure to an external small magnetic field. The mechanism of H_2O_2 enhancement upon the application of such magnetic field to the ferromagnetic electrocatalyst was elucidated through theoretical calculations and electron spin

density simulations.

2. Materials and methods

2.1. Chemicals and materials

2-Methylimidazole (Analytical reagent (AR), > 99.0 %, CAS: 693–98–1) was supplied by Aladdin Chemical Reagent. Cobalt nitrate hexahydrate (AR, > 99.0 %, CAS: 10026–22–9) and sodium sulfate (AR, > 99.0 %, CAS: 7757–82–6) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. Sulfamerazine (SMR, AR, > 99.0 %, CAS: 68–35–9) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Boron-doped diamond (BDD) anode with two active sides (single crystal silicon substrate, 10 mm × 20 mm × 2 mm) was purchased from Hu-nan New Frontier Science & Technology Ltd. Porous nickel foam (NF) substrate was obtained from Suzhou Maozhen New Material Technology Co., Ltd. Commercial neodymium magnets (100 mm × 50 mm × 20 mm) providing a 250 mT magnetic field were acquired from Shanghai Hao Magnetic Electromechanical Co., Ltd. A Tesla meter (ranging from 2 to 2400 mT) was acquired from Changsha Tunkia Measurement and Control Technology Co., Ltd., as measurement instrument to determine the magnetic field strength.

2.2. Preparation of ZIF-67-NF-T cathodes

NF was first cut into a size of 1 cm × 2 cm and then polished by sonication in 30 % aqueous hydrochloric acid for 15 min to remove metal oxides, then soaked in acetone for 24 h to remove organic matter, followed by 8 h in a blast drying oven. As shown in Fig. 1a, 20 mL deionized (DI) water with 18 mmol 2-methylimidazole and 20 mL DI

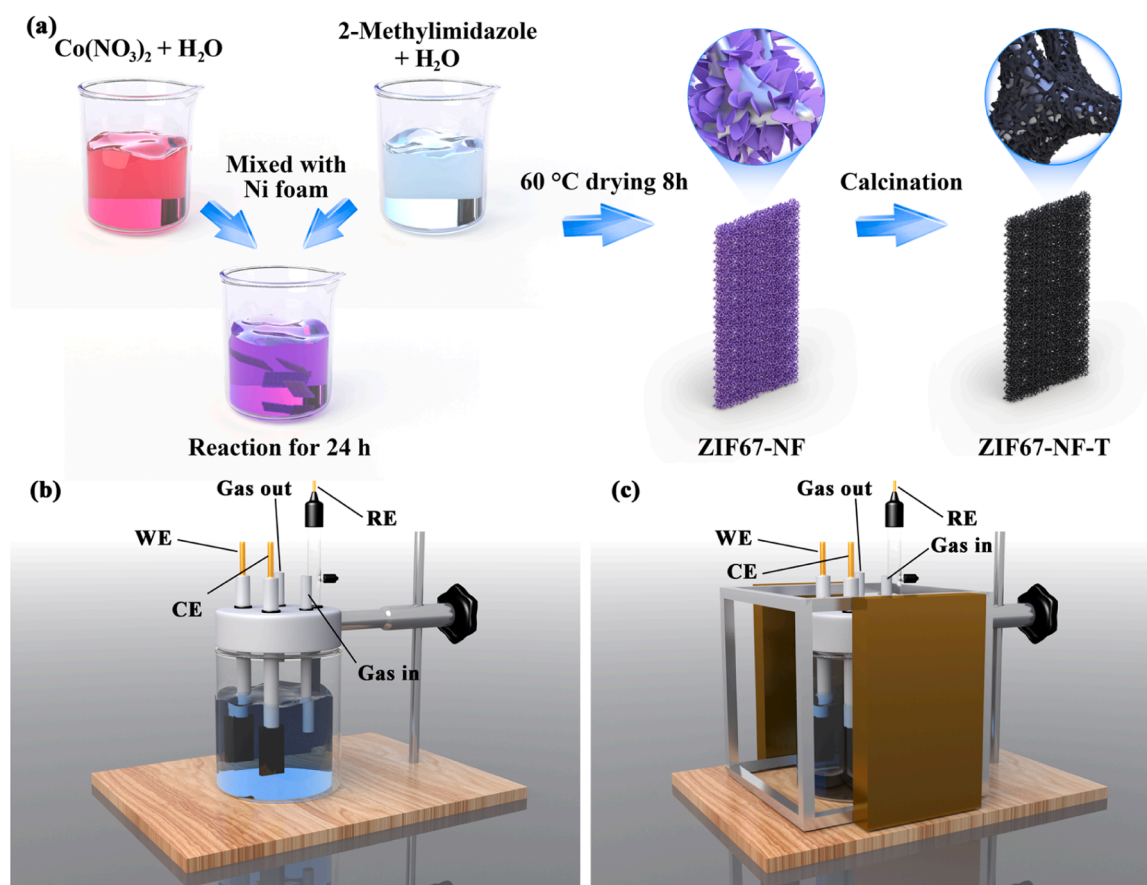


Fig. 1. (a) Synthesis route to obtain the modified cathodes. Set-up of the three-electrode electrochemical cell: (b) in the absence and (c) in the presence of a magnetic field provided by commercial Nd magnets.

water with 1.439 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ were mixed in a glass beaker, and then the mixture was stirred for 15 min until being totally dissolved. Four pre-treated NF pieces were added in the mixture and kept at 25 °C for 24 h, allowing and the ZIF67 precursors with metallic Co cores to grow on the NF substrates. Subsequently, clean purple ZIF67 ($\text{Co}/\text{Co}_3\text{O}_4$)-NF samples were obtained by rinsing with ethanol and DI water, followed by drying for 8 h. The samples were then calcined at different temperatures (300, 350, 400 and 450 °C) under N_2 flow for 120 min at heating rate of 5 °C min^{-1} . The samples, named as ZIF67-NF-T (T denotes the calcination temperature), were used as cathodes for the electrochemical trials.

2.3. Physicochemical characterization of ZIF-67-NF-T cathodes

X-ray diffraction (XRD) analysis was conducted using a D8 Advance diffractometer from Bruker, following Joint Committee on Powder Diffraction Standards (JCPDS) to determine the crystal phases. X-ray photoelectron spectroscopy (XPS) was conducted on American Thermo Scientific K-Alpha instrument to determine the valence states of the elements. Magnetic hysteresis loop (MHL) was measured with Lake-Shore7404 at ± 2 T. Scanning electron microscopy (SEM) images were obtained on a ZEISS Sigma500 microscope, while energy dispersive spectroscopy (EDS) was carried out using an Oxford Instruments X-Max device to assess the elemental distribution. The atomic spin orbital electron test was carried out using a German Bruker EMXplus-6/1 electron paramagnetic resonance (EPR) spectrometer.

2.4. Electrochemical techniques

Electrochemical characterization was performed on a workstation (CH Instruments Ins, CHI760E), employing a three-electrode cell with a working volume of 80 mL (working electrode: ZIF67-NF-T; counter electrode: BDD; reference electrode: saturated calomel electrode (SCE), as depicted in Fig. 1b and Fig. 1c. Tests with and without the application of an external magnetic field were conducted. The magnetic field was generated by two neodymium magnets positioned on both sides of the cell, ensuring parallel magnetic field lines. The magnetic field strength at the working electrode position was around 250 mT, as measured by a Tesla meter.

Cyclic voltammetry (CV) tests were performed on prepared cathode materials within a potential range from -0.8 V to $+0.4$ V vs SCE at a scan rate of 10 mV s^{-1} . Linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV s^{-1} . Both, LSV and CV tests were performance under O_2 or N_2 saturation. Electrochemical impedance spectroscopy (EIS) tests were carried out at the open circuit potential (OCP) across a frequency range of 10^5 to 10^{-2} Hz, using a sinusoidal disturbance amplitude of 10 mV. EIS data were analyzed using ZSimpWin v. 3.10 software (Echem, Lufkin, TX) to determine the charge transfer resistance (R_{ct}). Tafel slope tests were conducted over a range of OCP ± 250 mV.

2.5. Electrochemical H_2O_2 production and EF treatment

The H_2O_2 production tests via the 2e-ORR were conducted using a typical two-electrode cell, analogous to that shown in Figs. 1b and 1c but without including the reference electrode. In that setup, one of the ZIF67-NF-T pieces served as the working electrode and BDD as the counter electrode, with the current density maintained at 10 mA cm^{-2} . For the EF treatment, a concentration of 50 $\mu\text{mol L}^{-1}$ FeSO_4 was used to evaluate the performance of the magnetic field-enhanced EF system.

The H_2O_2 concentration analysis was performed using the potassium iodide-potassium hydrogen phthalate spectrophotometric method (see Text S1). The SMR concentration was determined by high-performance liquid chromatography (HPLC), with the detector set at a wavelength of 258 nm. The mobile phase was a mixture of acetonitrile and 0.1 % formic acid solution (v/v ratio 2:8), and the flow rate was set at 0.1 mL min^{-1} .

2.6. Density functional theory (DFT) calculations

DFT calculations were carried out using the Vienna Ab initio Simulation Package (VASP) [25,26]. The exchange-correlation potential was approximated using the Generalized Gradient Approximation (GGA) formulated by Perdew, Burke, and Ernzerhof (PBE) [27]. To address the interactions between ion cores and valence electrons, the Projector Augmented-Wave (PAW) method was employed [28]. DFT+U calculations were performed using the theoretical model proposed by Dudarev et al. [29]. A plane-wave cutoff energy of 500 eV was consistently maintained. The structural models underwent relaxation until the Hellmann-Feynman forces were reduced to less than -0.02 eV $\text{\AA}^{-1}$, and the energy change was minimized to less than 10^{-5} eV. For this relaxation process, the Brillouin zone was represented using a Γ -centered k-point grid of $10 \times 10 \times 10$. Additionally, Grimme's DFT-D3 method was utilized to accurately describe dispersion interactions among atoms in the adsorption models [30].

3. Results and discussion

3.1. Sample characterization

A series of characterization techniques was employed to analyze the structure, composition, morphology, and magnetic properties of the ZIF67-NF-T cathodes synthesized at four different temperatures in the range 300–450 °C. To analyze the composition and crystal structure of the synthesized ZIF67-NF-T cathode, XRD tests (Fig. 2) were first performed both on the as-synthesized cathode and those obtained by thermal treatment at various calcination temperatures (300, 350, 400 and 450 °C). The XRD diffraction peaks of the ZIF67 sample are displayed in Fig. 2a, highlighting the prominent crystal facets; specifically, peaks at around 10°, 13° and 18° correspond to (200), (211) and (222) planes that are typical of ZIF67 (CCDC 671073). As can be observed in Fig. 2b, calcination caused a noticeable shift in 2θ angles of these crystal facets, varying by approximately 2–3°. The thermal treatment resulted in carbonization, causing the disappearance of the (222) crystal facet and the emergence of a distinctive (310) crystal facet. Upon comparison of cathodes obtained at different carbonization temperatures, it can be concluded that the ZIF67-NF-350 sample, calcined at 350 °C, exhibited the highest level of crystallinity. Additionally, as the temperature increased, the excessive carbonization reduced the crystallinity, as evidenced by a decrease in the peak intensity.

The full XPS spectra of ZIF67-NF-T (300, 350, 400, and 450 °C) are showcased in Fig. 3a. The surface analysis of these samples revealed the presence of four dominant elements: carbon (C), oxygen (O), cobalt (Co), and nickel (Ni). The Co peaks predominantly stem from the oxidation of the Co centers, which are catalytic active sites within the ZIF67 MOF. The presence of carbon is attributed to the inherent carbon content of the metal-organic framework, whereas Ni originates from the NF metal substrate. These results compellingly confirm the successful integration of the magnetic ZIF67 material onto the substrate [31].

To gain a more detailed understanding the elemental states, first we conducted a deconvolution of the XPS fine spectra of the ZIF67-NF-350 sample. For the C 1s spectrum (Fig. 3b), deconvolution revealed two distinct peaks: one at approximately 284.6 eV, which originated from C-C sp^2 derived from the organic framework of ZIF67; this peak was primarily related to the benzene-like structure within 2-methylimidazole, a crucial precursor in the synthesis, which upon carbonization evolved into the C-C sp^2 configuration. Another peak, observed at around 288.9 eV, was interpreted as the C-O characteristic peak, likely stemming from the incorporation of oxygen during the calcination process. When analyzing the Co 2p spectrum (Fig. 3c), our deconvolution procedure allowed distinguishing two spin-orbit double peaks and two associated vibrational satellite peaks, located near 780 eV ($2\text{p}_{3/2}$) and 795 eV ($2\text{p}_{1/2}$), respectively. The spin-orbit double peaks suggest the presence of Co in multiple valence states, particularly correlating to the

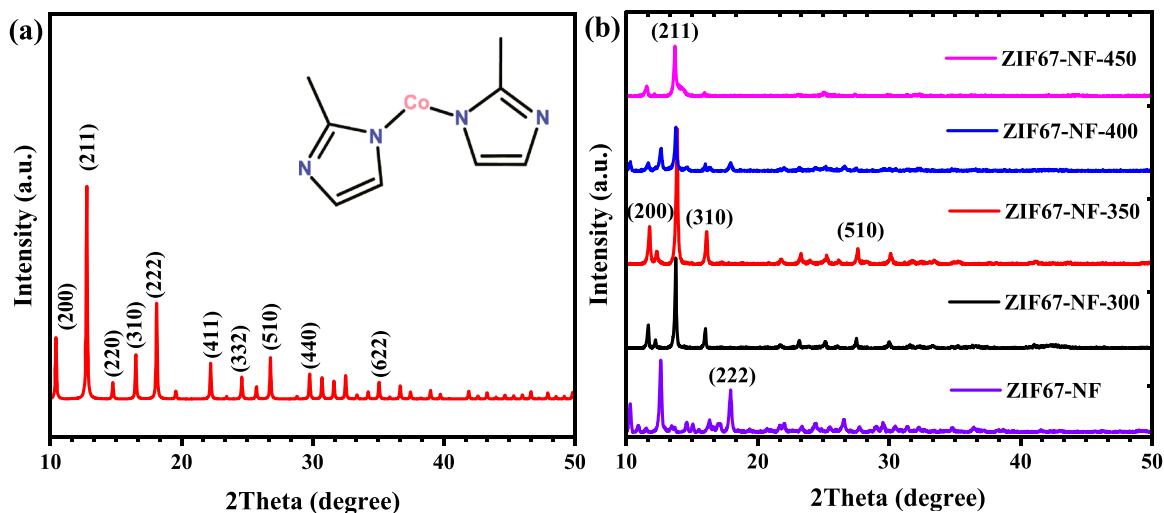


Fig. 2. XRD patterns of: (a) Standard ZIF67 and (b) ZIF67-NF-T (T: 300, 350, 400 and 450 °C).

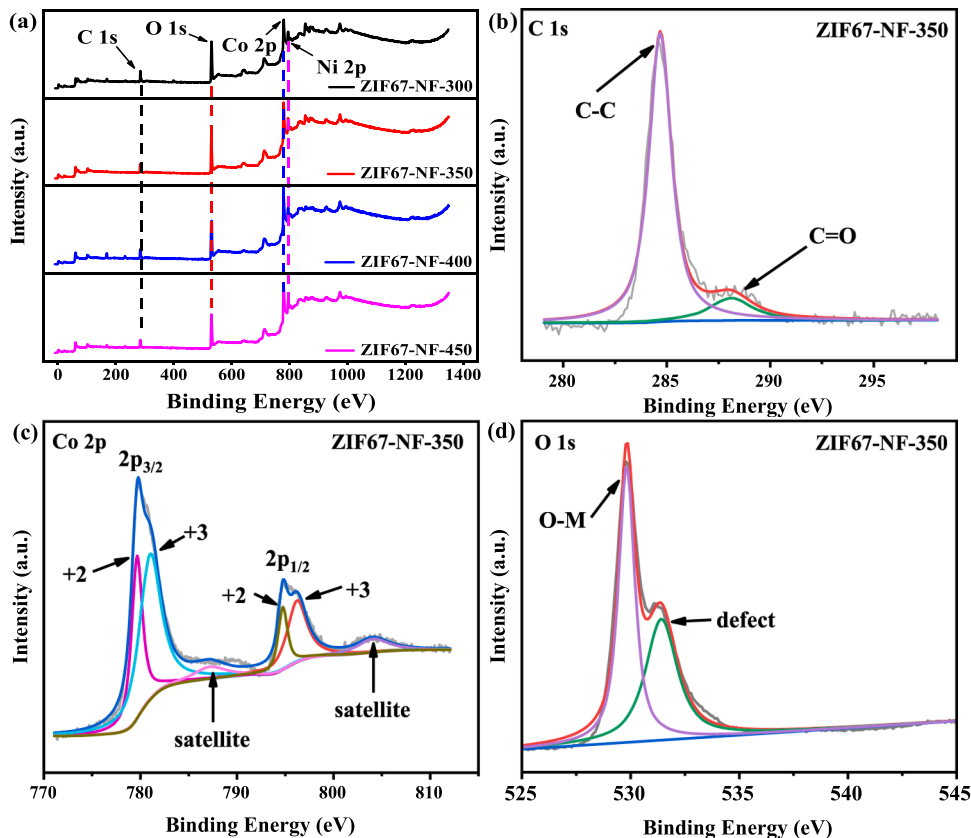


Fig. 3. (a) XPS survey spectra for ZIF67-NF-T (T: 300, 350, 400 and 450 °C). High resolution XPS spectra of ZIF67-NF-350, showing the deconvoluted peaks for (b) C 1s, (c) Co 2p and (d) O 1s.

+2 valence and +3 valence states in Co_3O_4 .

The high-resolution XPS spectrum of O 1s revealed the presence of two distinct oxygen species (Fig. 3d). The peak located at 529.5 eV corresponded to a typical O-metal bond, indicative of standard oxygen coordination with metal atoms. In contrast, the peak at 531.1 eV was indicative of the oxygen species at defect sites, characterized by lower coordination numbers, a common feature in materials with small dimensions. In the context of ZIF67, these oxygen species primarily originated from the interaction between carbon elements within the metal-organic framework and oxygen.

Note that Fig. S2 summarizes the high-resolution XPS spectra for ZIF67-NF-T at all other temperatures, in addition to Ni 2p spectrum at 350 °C. Regarding the Ni 2p analysis, similar deconvolution methods yielded two vibrational satellite peaks along with their corresponding $2p_{3/2}$ and $2p_{1/2}$ spin-orbit peaks [32]. Notably, as the temperature increased beyond 350 °C, a significant decrease was observed in the peak area related to the +2 valence orbital of Ni. This trend indicated a potential instability of Ni in the +2 valence state at high temperatures, suggesting a transformation to the more thermally stable +3 valence state [33].

Worth mentioning, during the deconvolution of spectra from cathodes obtained at 400 °C, there was a noticeable increase in the proportion of oxygen species at these low coordination sites (Fig. S2). This increase is primarily attributed to the transformation of Ni elements from the +2 valence state to the +3 valence state, resulting in fewer O atoms being coordinated with Ni. This shift led to the release of loosely bound oxygen atoms, which subsequently interacted with carbon elements, thereby increasing the proportion of low oxygen coordination sites [34]. However, as the temperature was further elevated to 450 °C, the cathode composition underwent a compositional stabilization. This shift towards greater stability leads to the disintegration of these less stable oxygen configurations, gradually restoring the proportion of oxygen species to its previous, more stable state [35].

SEM images were used to study the initial structure of ZIF67 prior to grow it on the NF. As depicted in Fig. 4a, the ZIF67 samples prepared with deionized water exhibited a unique nano-spindle array structure, characterized by a significantly higher aspect ratio compared to the conventional rhombic dodecahedral morphology synthesized using methanol. This observation aligns with existing literature, which suggests that nanomaterials with higher aspect ratios typically demonstrate improved electron transport properties [32,36]. SEM images thus provide crucial insights into the morphological variations induced by the choice of solvent in the synthesis of ZIF67, highlighting the impact of these changes on the material physical properties and potential applications [37]. Subsequent SEM analysis was performed for the in-situ grown ZIF67 on NF substrate, as well as for the post-calcination electrode materials. Fig. 4b showcases the vertically aligned in-situ growth ZIF67, demonstrating a well-organized and directional growth pattern. The initiation of this in situ growth process in the liquid phase begins with the deprotonation of the 2-methylimidazole ligand, leading to the generation of H^+ ions. These protons interact with the NF substrate, facilitating the release of Ni^{2+} ions. Subsequently, these Ni^{2+} ions serve

as anchoring points for the 2-methylimidazole molecules on the NF surface, promoting the nucleation and subsequent in-situ growth of ZIF67 precursor directly on the substrate. Following this initial nucleation phase, a coordinated synthesis reaction occurs involving 2-methylimidazole and cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$). This reaction sequence is akin to an induced self-assembly process, culminating in the formation of the ZIF67 structures directly on the NF surface. The resultant morphology, as vividly depicted in Fig. 4b, is a testament to the efficacy of this synthesis approach, which enables the direct and ordered growth of ZIF67 on NF, thus potentially enhancing the cathode overall performance in its intended applications.

Fig. 4c-f display the morphology of cathodes subjected to calcination at various temperatures (300–450 °C). Post-calcination, the ZIF67, which underwent in-situ growth on the NF surface, displayed a skeleton structure. This was attributed to the carbonization of its organic components under elevated temperatures, leading to a dendritic morphology characterized by extensive interconnectivity on the substrate, as seen in Fig. 4c. At this stage, the presence of fusiform structures suggested that the desired calcination temperature was yet to be fully achieved, with the formation of a complete interlinked metal-organic skeleton still in progress and the pore structure remaining indistinct. Upon increasing the calcination temperature to 350 °C, the cathode surface achieved complete fusiform carbonization, resulting in a well-defined skeletal structure with enhanced cross-linking, as depicted in Fig. 4d. Moving to Fig. 4e, the fully carbonized organic framework exhibited a trend towards reduced pore size compared to the structure in Fig. 4d, leading to a less pronounced structural definition. However, at the most extreme calcination temperature of 450 °C, as shown in Fig. 4f, the metal-organic framework collapsed. This collapse, occurring post-carbonization, resulted in the accumulation of ZIF67 on the carrier's surface, which adversely impacted both electron and reactant mass transfer during electrochemical reactions. Consequently, this

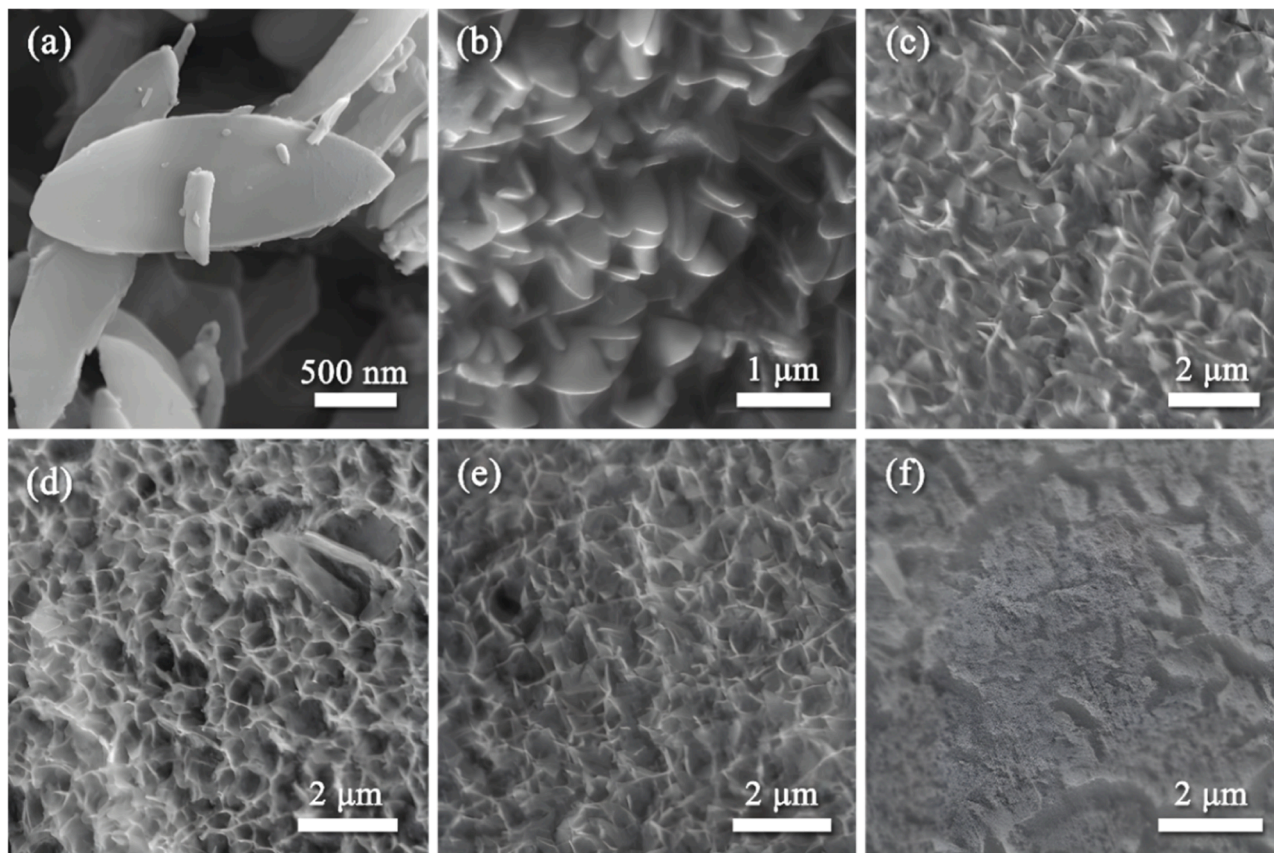


Fig. 4. SEM images of: (a) ZIF67 powder, (b) ZIF67-NF, (c) ZIF67-NF-300, (d) ZIF67-NF-350, (e) ZIF67-NF-400, and (f) ZIF67-NF-450.

accumulation is expected to pose significant challenges to efficient electron transfer and reactant diffusion, leading to a decrease in the activity of the electrode material.

3.2. Superior ORR performance of ZIF67-NF-T cathodes exposed to a magnetic field

To investigate the ORR performance of the four electrodes and the effect of the magnetic field on their ORR activity, CV tests were conducted in the presence and absence of a magnetic field, as shown in Fig. 5. CV tests were initially conducted under both O_2 -saturated and O_2 -free (i.e., N_2 -saturated) conditions to establish the potential window for ORR, which was set between -0.8 V and $+0.4$ V vs SCE. The results revealed distinct oxidation and reduction peaks at approximately 0.1 V and -0.6 V vs SCE, respectively, under O_2 -saturated conditions, as shown in Fig. S3a and S3b. Notably, the reduction peak disappeared in the O_2 -free media (Fig. S3c and S3d), evidencing its direct association with the ORR.

The influence of the magnetic field on the voltammetric profiles of the four ZIF67-NF-T working electrodes can be observed in Fig. 5. Regarding the ORR response in the O_2 -saturated electrolyte, it is clear that the ZIF67-NF-350 sample exhibited the highest current density under both conditions, with and without the magnetic field (Fig. 5). It means that, among the four cathodes, this one showed the highest ORR activity and, furthermore, its performance could be further enhanced in the presence of 250 mT magnetic field. On the other hand, it is worth to note that the magnetic field significantly enhanced not only the reduction signal but also the oxidation one, which will be discussed below.

Once ascertained the superior ORR activity of the ZIF67-NF-350 electrode and the beneficial impact of the magnetic field, it is necessary to explore the reasons. Detailed mechanisms and discussions are presented in the subsequent sections.

3.3. Correlation between physicochemical and magnetic properties of the ZIF67-NF-T cathodes

This superior performance of the ZIF67-NF-350 cathode is attributed to its optimal metal-organic framework structure. Specifically, the framework, created by coating magnetic ZIF67 with cobalt as the active metal center on NF at 350 °C, provides an ideal arrangement for the reaction. The dendritic, cross-linked organic framework promotes the exposure of reactive sites for ORR. As evidenced in SEM images (Fig. 4),

such a structure enhances the adsorption, binding, and desorption of O_2 on the ZIF67-NF-350 surface. Worth highlighting, the CV curve of the sample calcined at 450 °C showed different trends compared to the other cathodes. This deviation is likely due to the high calcination temperature, which altered the metallic NF substrate, as also reflected by the XPS analysis (Fig. 3 and S2).

To investigate the ferromagnetic properties and magnetization response of the cathodes obtained at different temperatures, MHL tests were carried out. The profiles obtained from a long-range magnetic field intensity scanning, from -25 kG to 25 kG, are depicted in Figs. 6a and 6b. The classical symmetric closed S-shaped and obvious magnetic induction phenomenon profiles confirmed the ferromagnetic nature for these cathodes. Short-range scanning, obtained from -60 G to 60 G, are shown in Fig. 6b. The corresponding fitting yielded the remanence (i.e., the residual magnetization once the external magnetic field is removed) and coercivity (i.e., the magnitude of the required field needed to remove all magnetization) values, which are specified in Table S1 and represented in Fig. 6c for a more clear understanding of their trends with the calcination temperature. From the remanent magnetic induction to coercive force ratio, it can be concluded that the materials were characterized as close to hard magnetic (i.e., permanent magnet). It means that once magnetized, these ZIF67-NF-T cathodes retain their magnetic properties even after the external magnetizing force is removed. In addition, the values of the grain diameter along the direction perpendicular to the (210) crystal plane at different temperatures are summarized in Table S2 and represented in Fig. 6d. The (210) crystal plane was the dominant exposed facet, as indicated by the XRD data (Fig. 2).

Based on the study of the dependence of the fitted Br, Hc, and grain diameter with the calcination temperature, it is evident that from 300 to 350 °C, the coercivity rises as the grain size increases. The homogenization process enhances the magnetic resistance, making the movement of magnetic domain walls more difficult. Despite the slight remanence decrease, the increase and homogenization of grain size favors the optimization of the magnetic structure, improving the conductivity and activity. With further increases in thermal treatment temperature up to 400 °C, the coercivity reaches its peak, forming a stable magnetic domain structure, which is mainly reflected in a slight decrease in grain diameter. At higher temperature, grain growth as well as plausible partial oxidation leads to an increase in internal defects, weakening the magnetic resistance, reducing the magnetic coupling between grains, and eventually affecting the magnetic properties. This trend can also serve to justify the voltammetric responses observed in Fig. 5, where the

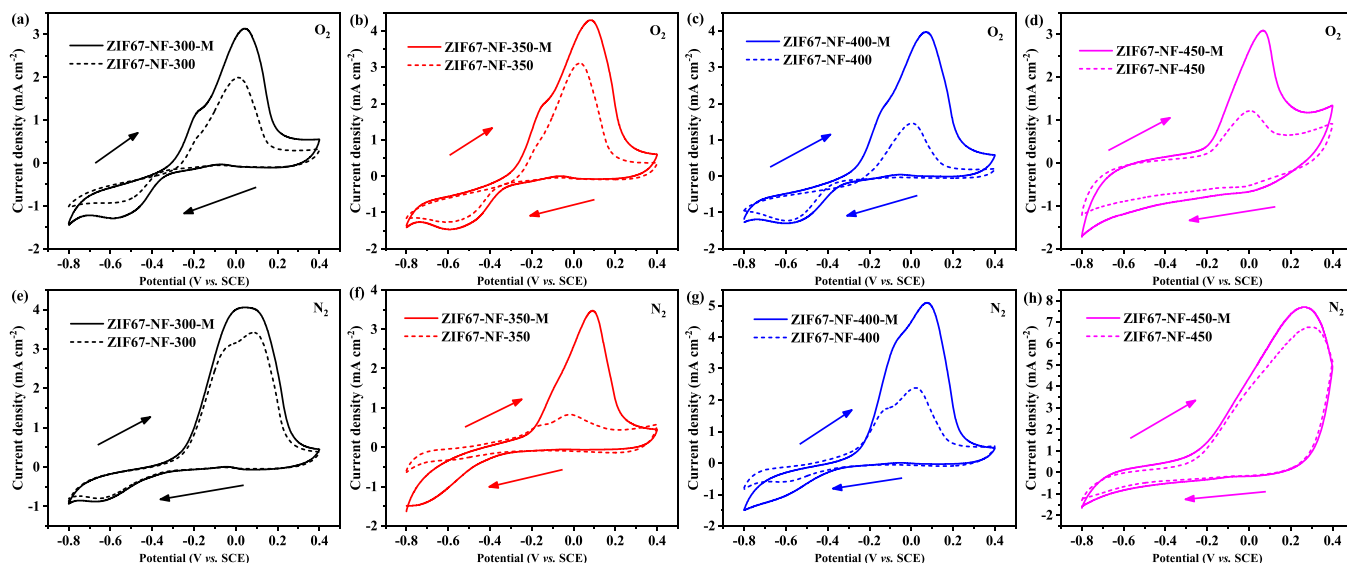


Fig. 5. Influence of magnetic field (M) on cyclic voltammograms for ZIF67-NF-T (T denotes calcination temperature: 300, 350, 400 and 450 °C) in (a-d) O_2 -saturated and (e-h) N_2 -saturated electrolyte.

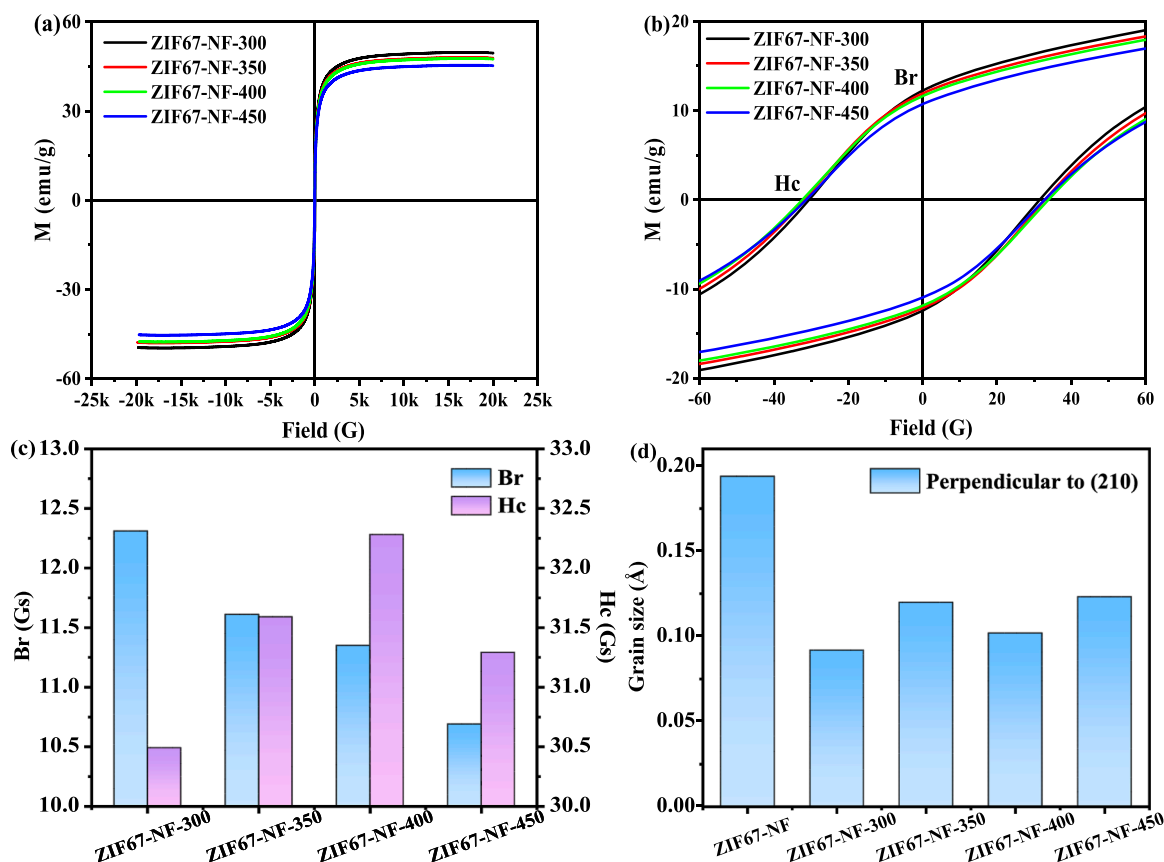


Fig. 6. Magnetic hysteresis loop of ZIF67-NF-T (T: 300, 350, 400 and 450 °C) for (a) long-range magnetic field intensity scanning (from -25 kG to 25 kG) and (b) short-range scanning (from -60 G to 60 G); (c) Fitting data of Br and Hc obtained from (a), and (b); (d) Sample grain diameter along the direction perpendicular to the (210) crystal plane for different cathodes.

ORR signal of the electrode obtained at the highest temperature was comparatively lower.

The ZIF67-NF electrode produced at 350 °C achieved an optimal state in terms of coercivity, remanence, grain size, structure, and composition, thereby exhibiting excellent ORR performance under both magnetic and non-magnetic conditions, which outperformed the other three electrodes. At 450 °C, in particular, the excessively high temperature led to grain growth and oxidation, negatively affecting the magnetic properties and hence, the ORR performance. Based on this, the ZIF67-NF-350 cathode was selected to further investigate the mechanisms behind the enhanced ORR activity upon the introduction of a magnetic field.

3.4. Mechanism of enhanced ORR activity upon the introduction of a magnetic field

The effects of a magnetic field on ORR can be explained through two main mechanisms: mass transport (hydrodynamic effect) and kinetics (electrocatalytic effect). In non-magnetic electrodes, the application of a uniform magnetic field affects the charged species, such as the electrolytes, through the Lorentz force [38]. When the magnetic field and electric current directions are not parallel, magnetohydrodynamic (MHD) effects create localized disturbances that enhance the mass transport (i.e., magnetohydrodynamic flow) of ORR reactants and products. In magnetic electrodes, the magnetic field also alters the number of electrons occupied in e_g -orbitals, reducing the energy barrier for electron transfer. This alignment enhances the electrochemical kinetics, as proven for hydrogen evolution reaction [39], and hence, the ORR kinetics could also be improved following a similar phenomenon.

To understand the mechanism of an external magnetic field for boosting the ORR rate, CV and LSV tests were conducted, as shown in Figs. 7a and 7b. These tests compare the performance of different materials, including a bare NF substrate, under O_2 -saturated conditions with and without an applied magnetic field. To exclude the contribution of MHD caused by the Lorentz force, the electrochemical characterization of a titanium foam (TF) with a structure analogous to NF, but lacking its magnetic properties, is also compared in Fig. 7a. It can be observed that the voltammograms recorded using the non-magnetic TF cathode exhibited no significant changes within the ORR potential range when the magnetic field was applied. This implies that the possible magnetic enhancement of ORR rate is not primarily due to the improved mass transport of reactants/products, but rather the influence of the magnetic field on the number of electrons occupying the e_g -orbitals in Co ions, thereby impacting the electrochemical kinetics. Therefore, one crucial prerequisite for cathodes to achieve an ORR enhancement by external magnetic fields is to possess inherent ferromagnetic properties. This premise is further supported by the results for the NF substrate (Fig. 7a), which also showed a greater current density in the presence of the magnetic field. This comparison underscores the unique magneto-electric effects in magnetic cathode materials like ZIF67-NF-350. The selection of a Ni-based substrate for ZIF coating, as opposed to Ti, was made to minimize the magnetic gap between the substrate and the ZIF layer. Using a non-magnetic substrate such as Ti would create a significant magnetic disparity between the electrodes before and after ZIF loading, potentially leading to substantial differences in the impact of the magnetic field on O_2 mass transport within the system. Such disparity could result in less consistent and efficient performance. By employing a magnetic substrate like NF, the magnetic gap is minimized,

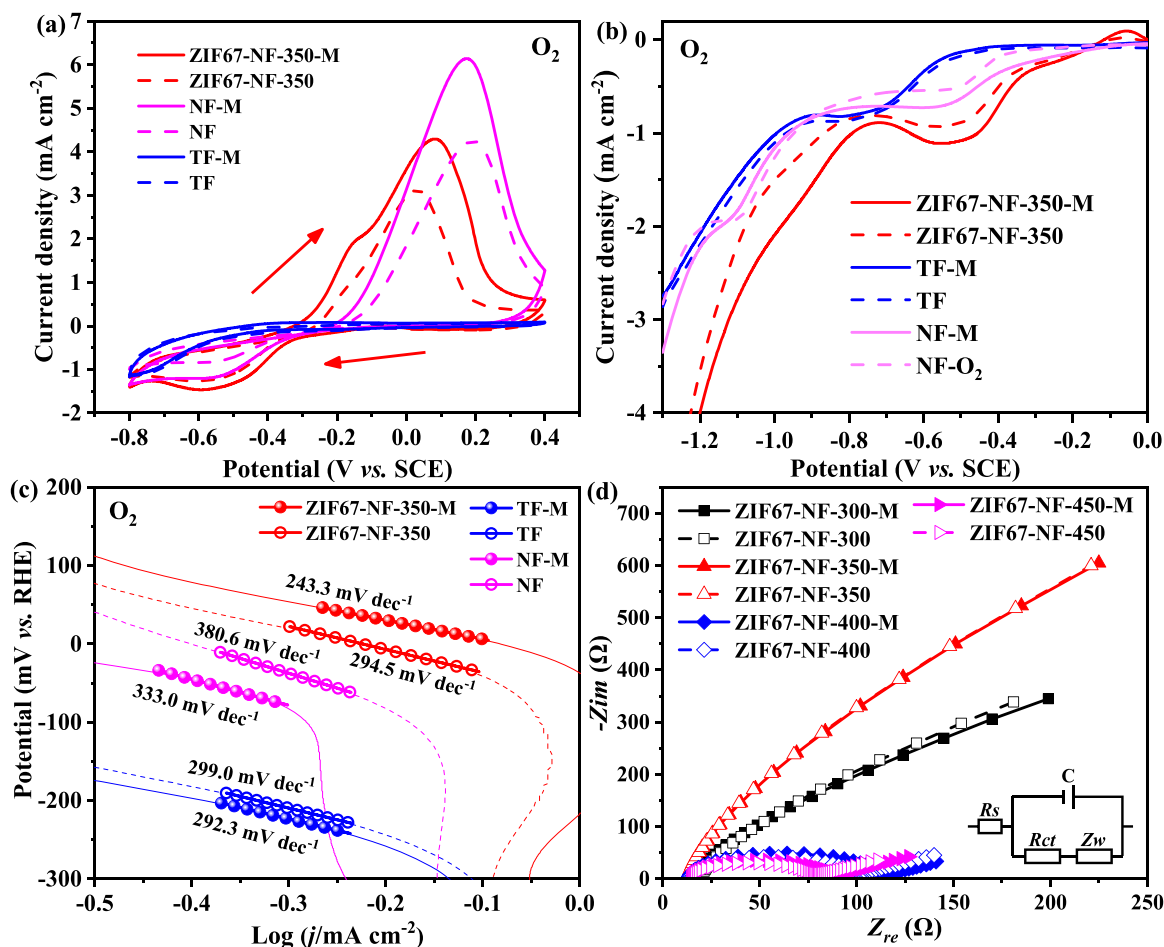


Fig. 7. (a) Cyclic voltammograms of ZIF67-NF-350, NF and Ti foam in O_2 -saturated 0.1 M Na_2SO_4 solution, in some cases in the presence of an external magnetic field (M). (b) Analogous to plot (a) but in linear sweep voltammetry mode. (c) Tafel slope curves of the three materials, obtained from results of plot (b). (d) Nyquist plot for ZIF67-NF-T (T: 300, 350, 400 and 450 $^{\circ}C$), in the presence of M in some cases, and equivalent circuit (inset).

ensuring a more uniform magnetic response that is primarily influenced by the ZIF coating, thereby enhancing the overall effectiveness of the magnetic field on the O_2 mass transport.

It is worth remarking that the magnetic field significantly enhanced both the reduction and oxidation signals, indicating that the magnetic field can simultaneously boost different types of electrochemical reactions. Therefore, the enhancement by magnetic fields is not only applicable to ORR. Interestingly, the magnetic field also led to the appearance of a novel oxidation peak around -0.15 V (Fig. 7a), which can also be found for ZIF67-NF-300 and ZIF67-NF-400 (Figs. 5a, 5c) [38]. This new peak could be attributed to the magnetic field-induced increase in the number of electrons in the e_g -orbitals of Co ions, providing more active electrons that participate in σ -bonding with intermediates and facilitate the charge transfer at the catalytic interface. The magnetic field may be facilitating a novel oxidation process or enhancing a previously unobservable oxidation state transition, resulting in the emergence of this additional peak. Note that the ZIF67-NF-450 cathode did not show this new oxidation peak, probably due to structural changes caused at high temperature. To further explore the magnetic field effects on ORR, displaying a peak at around -0.6 V, LSV tests were conducted from 0 to -1.2 V vs. SCE (Fig. 7b for ZIF67-NF-350, and Fig. S4 for the other three electrodes), supporting the insights obtained from CVs. LSV results showed no changes for the non-magnetic TF cathode under a magnetic field. However, magnetic cathodes like NF and ZIF67-NF-350 showed the expected enhanced ORR performance under a magnetic field. The ZIF67-NF-350 cathode showed a higher ORR

performance as compared to NF, even in the absence of the magnetic field, highlighting the positive contribution of ZIF67 incorporation. Further amelioration was achieved under the magnetic field. In contrast, ZIF67-NF-450 showed reduced ORR activity and no clear ORR reduction peak, likely due to the coating degradation from high temperature (Fig. S4), also confirming the comparatively minor effect of the magnetic field shown in CV tests (Fig. 5).

The influence of the magnetic field on the electronic structure, specifically the increased occupancy of e_g -orbitals and the subsequent alteration of spin states, can also be reflected on the Tafel slope and exchange current density (Fig. 7c). The Tafel slopes for the magnetic NF substrate and ZIF67-NF-350 cathode significantly decreased with the introduction of a magnetic field, from 380.6 to 333.0 $mV\ dec^{-1}$ for the former material and from 294.5 to 243.3 $mV\ dec^{-1}$ for the latter, thus corroborating the magnetoelectrocatalytic effect on the ORR. In contrast, non-ferromagnetic TF electrode showed negligible change when exposed to a magnetic field, confirming the need of ferromagnetic properties to benefit from external magnetic fields. Impedance tests were also performed, interpreting the results using Nyquist plots fitted with an equivalent circuit model (Fig. 7d). The ZIF67-NF-350 cathode showed the lowest charge transfer resistance (R_{ct}) among all samples (Table S3), likely due to the varying levels of carbonization in the ZIF67 organic framework that resulted from the different calcination temperatures. An increased exposure of the Co metal center in ZIF67-NF-350 facilitated a more efficient electron transfer, leading to a reduced R_{ct} [39].

For the magnetic electrodes, much lower R_{ct} values were obtained, since the magnetic field increases the number of electrons in the high-energy level e_g -orbitals of Co ions, with the subsequent alteration of spin states. Therefore, more active electrons participate in σ -bonding with intermediates and facilitate charge transfer at the catalytic interface.

3.5. Simulations and experiment evidence of magnetically-altered e_g -orbital occupancy

As mentioned above, we hypothesize that the magnetic field increases the occupancy of the high-energy e_g -orbitals of Co ions, leading to alterations in spin states and resulting in an enhanced ORR performance of the ferromagnetic ZIF67-NF-T samples. First, density of states (DOS) calculations were conducted on the Co/Co₃O₄ component, the main constituent of the ZIF67-NF-T. These calculations were analyzed both before and after the magnetization, in order to examine the change in the number of electrons and the electron spin interactions (Fig. 8).

Before magnetization, the Co 3d and O 2p orbitals in Co₃O₄ showed

parallel alignment at the Fermi level, indicating low occupancy of high-energy e_g -orbitals and a low-spin state. After magnetization, increased orbital overlapping suggests higher occupancy of the high-energy e_g -orbitals and enhanced spin polarization, facilitating the electron transfer in Co-O bonds [40]. Simulation results show that the ligand field at Co sites in Co₃O₄ increases from 0.114 to 0.276 μ B post-magnetization, suggesting that 3d-2p hybridization boosts the charge transfer and accelerates the ORR [41]. VASP simulations of electron spin density before and after magnetization (Fig. 8c and 8f) demonstrate a significant increase in spin density upon magnetization, indicating a higher energy state and greater activity. This higher spin density can be related to a greater occupancy of the high-energy e_g -orbitals, enhancing their participation in electron transfer and promoting the ORR [19]. Finally, our experimental results indirectly confirmed that the magnetic field regulates the electron occupancy in the e_g -orbitals (Fig. 8i).

Based on these results, a mechanism for magnetic field-enhanced 2 e^- ORR is proposed in Fig. 8g–j [42,43].

Upon magnetization, the alignment of magnetic moments increases the electron occupancy in the high-energy e_g -orbitals of Co ions,

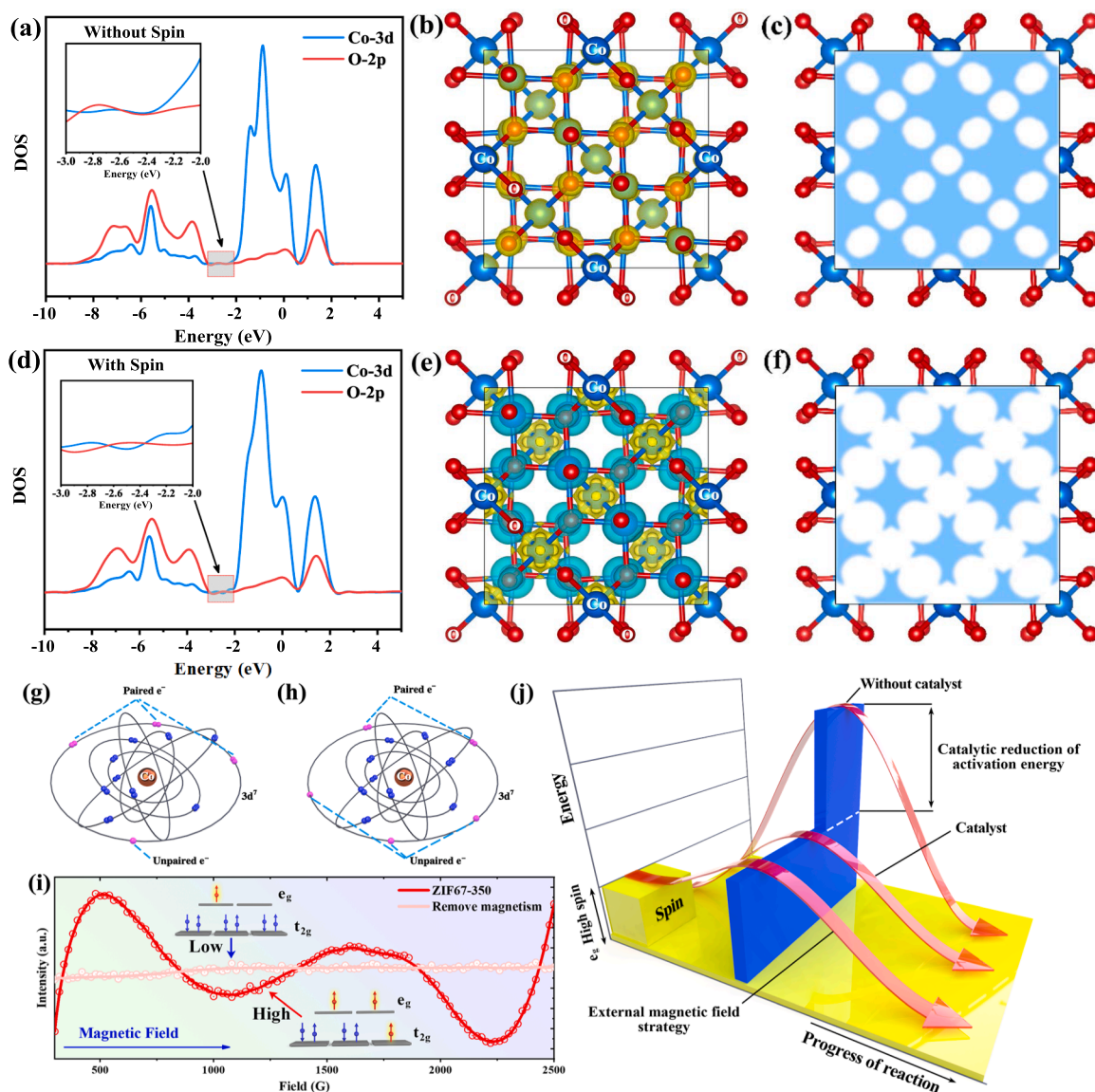


Fig. 8. Estimated density of states (DOS) of Co/Co₃O₄ (a) without spin and (d) with spin. The corresponding computational models are respectively depicted in image (b) and (e). The simulated electron spin density map is shown in (c) and (f), respectively. Outer electron orbitals of Co atoms (g) without and (h) with (i.e., high-spin state) magnetization. (i) Measurement of the number of electrons occupying the e_g orbitals under magnetic field. (j) Schematic diagram of the mechanism by which high-spin state electrodes enhance the 2 e^- -ORR and hence, the EF performance in the presence of a magnetic field.

significantly enhancing the spin density without electron exchange with the external environment. According to atomic orbital theory, cobalt typically has three paired and one unpaired electron in its outermost 3d orbital. Magnetization induces a high-spin state in Co, splitting one paired electron into two unpaired electrons, resulting in two paired electrons and three unpaired electrons (Fig. 8g and 8h) [44]. The increase in unpaired electrons in the e_g -orbitals accounts for the higher electron spin density observed in our models, leading to increased electron instability (Fig. 8i) and elevating the intrinsic energy of the cathode. From the electron spin test of Fig. 8i, it can be seen that with the change of the magnetic field, the magnetic sample has a stronger vibration of the upper and lower absorption values; conversely, after the removal of the field, no significant vibration could be observed. This phenomenon indicates that the magnetic field has a significant spin vibration effect on the outermost electrons of the magnetic material [45]. Consequently, the magnetized ZIF67-NF-350 cathode, with increased electron occupancy in the e_g -orbitals and a high-spin state, possesses higher initial energy, reducing the activation energy required for the ORR. This mechanism explains the enhanced ORR activity of ferromagnetic materials upon magnetization (Fig. 8j).

3.6. Magnetic field-enhanced H_2O_2 yield and SMR decay in EF treatment

To gain a thorough understanding of the possible H_2O_2 yield enhancement using the four magnetic ZIF67-NF-T cathodes under a

magnetic field, from an application point of view, the accumulation of H_2O_2 concentration and the degradation of SMR antibiotic by EF process were studied, comparing the effect of an applied magnetic field (Fig. 9a-d). During H_2O_2 electrogeneration (Eq. 1), samples were collected every 10 min during the first hour and every 30 min between 60 and 120 min. The profiles revealed a linear increase in the electrochemical H_2O_2 accumulation until 60 min, followed by a plateau due to a balance between the H_2O_2 production and its consumption (Fig. 9a and Fig. S5a). Among these cathodes, ZIF67-NF-350, calcined at 350 °C, clearly showed the highest H_2O_2 production, reaching 0.289 mM at 120 min of electrolysis. When subjected to a magnetic field, the H_2O_2 concentration reach 0.463 mM, accounting for 62.3 % rise after 120 min as compared to the absence of the magnetic field. Following the above explanations, this improvement can be attributed to the enhanced cathode reactivity in terms of facilitated ORR. The current efficiency (CE) increased significantly upon magnetization, reaching a maximum of 46.5 %, accounting for a 60.5 % improvement as compared to pre-magnetization (Fig. 9b). Higher CE means lower electric charge required for reaching a given H_2O_2 yield, thereby reducing the energy consumption in an effective and inexpensive way.

To evaluate the SMR pollutant degradation by homogeneous EF process, a solution of 50 mg·L⁻¹ SMR + 50 mM Na₂SO₄ + 50 μM FeSO₄ at pH 3 was employed, carrying out 180 min electrolytic assays at 20 mA and room temperature. Samples were collected every 30 min, and the normalized antibiotic concentration decays are depicted in

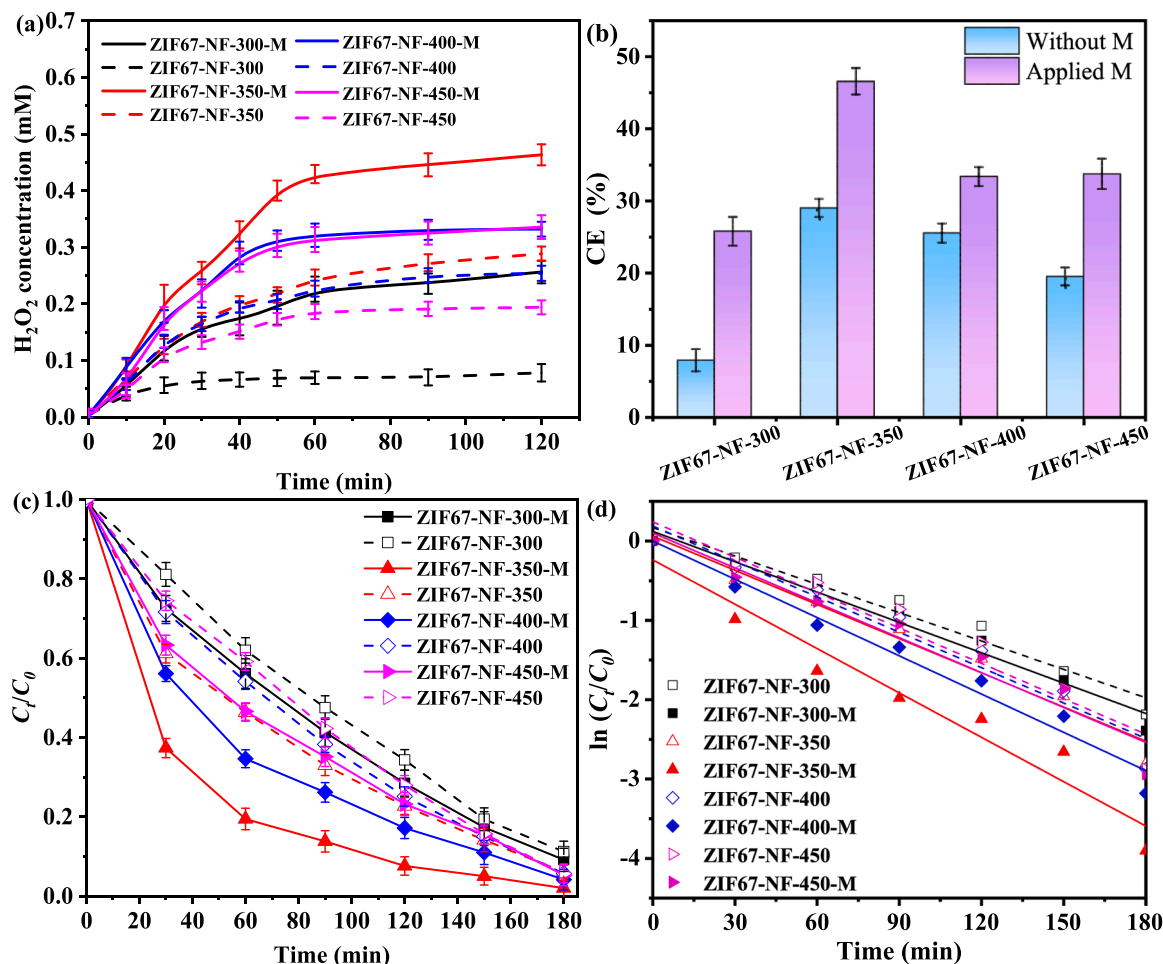


Fig. 9. (a) H_2O_2 generation with different cathodes, in the absence and presence of an external magnetic field (M). (b) Current efficiency determined from results of plot (a) at 120 min. (c) Normalized SMR concentration decay using the different electrodes in the presence and absence of M. (d) Corresponding kinetic analysis of decays shown in plot (c). Conditions: 50 mM Na₂SO₄, pH 3, current density of 10 mA cm⁻², air flow rate of 300 mL min⁻¹; the solutions contained 50 μmol L⁻¹ FeSO₄ in EF trials of plot c.

Fig. 9c and Fig. S5b. As can be seen, in all cases the antibiotic could be almost completely degraded at 180 min, which confirms the great catalytic ability of the Co-based coating to produce the $\cdot\text{OH}$ precursor (i.e., H_2O_2). The EF treatment with the ZIF67-NF-350 cathode witnessed the most significant improvement in pollutant degradation efficiency after magnetization (i.e., approximately 50 % enhancement), with over 80 % and 92 % degradation already achieved at 90 and 120 min (Fig. S6), respectively, thanks to the efficient production of hydroxyl radicals (Eq. 2). In fact, the drug disappearance with this cathode was very fast during the first 60 min, whereupon the degradation rate decreased to some extent, owing to a depletion of SMR molecules that favors the parasitic reactions (i.e., $\cdot\text{OH}$ self-consumption). The drug concentration decays were more gradual using the other cathodes (either uncoated or coated NF), corroborating the importance of the spin state to activate the ORR. All the degradation kinetics matched perfectly to a pseudo-first-order, as depicted in Fig. 9d. The observed rate constant (k_{obs}) for the magnetized ferromagnetic electrodes showed a clear improvement as compared to the value in the absence of magnetic field, as shown in Table S4, confirming that magnetization enhanced the reduction rate in the EF reaction and accelerated the overall degradation process.

4. Conclusions

For the very first time, this study demonstrates from a fundamental point of view the magnetic field-enhanced 2e^- ORR, as well as its application to boost the EF process, employing a magnetized ferromagnetic NF/ZIF67 cathode. This strategy allows addressing the slow oxidation encountered in systems with inherently low H_2O_2 production. The magnetized cathode allowed attaining a substantial increase in H_2O_2 electrosynthesis (over 60 %), leading to over a 50 % acceleration of an antibiotic degradation. The enhanced H_2O_2 yield is attributed to the greater e_g -occupancy of electrons of Co ions upon magnetization, rather than to a magnetohydrodynamic effect. This work is expected to contribute to the development of more efficient advanced water decontamination systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 52070056, No. 52000052) and State Key Laboratory of Urban Water Resource and Environment (Harbin Institute of Technology, No. 2024TS15), National Key R&D Program of China, Ministry of Science and Technology, (No. YS2023YFC3900124 and 2023YFC3905603), Ministry of Education's Chunhui-Project Cooperative Scientific Research Project (No. 202200482) and Heilongjiang Province Key R&D Plan (No. 2022ZX02C18). I. S. is grateful to projects PID2022-140378OB-I00 (MICIU/AEI/10.13039/501100011033, Spain), co-funded by ERDF/EU and 2021SGR00596 (AGAUR, Generalitat de Catalunya).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2025.125149](https://doi.org/10.1016/j.apcatb.2025.125149).

Data availability

Data will be made available on request.

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