



Thermal Conversion of Cobalt Based Hexacyanoferrates into Derived Cobalt Oxides for Supercapacitor Applications

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Abstract

We report the synthesis of cobalt-based hexacyanoferrate (Co-HCF) via a simple co-precipitation method and its subsequent conversion to a derived oxide through thermal treatment. Comprehensive characterization was performed using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). XRD confirms the cubic crystal structure corresponding well to the JCPDS card no. 00-024-0327. FTIR confirms the presence of functional groups in Co-HCF, while the annealing process results in the complete removal of the cyanide ligands, yielding the derived oxide. SEM and EDX analyses confirm the cubic morphology and elemental composition of the prepared samples. Furthermore, electrochemical evaluation using

cyclic voltammetry (CV) revealed that Co-HCF delivered a higher specific capacitance (C_s) of 624 F g^{-1} at 5 mV s^{-1} , highlighting pseudocapacitive behavior due to its open framework structure and abundant redox-active cobalt centers. In contrast, the annealed sample exhibited comparatively lower C_s of 143 F g^{-1} under identical conditions, attributed to the partial collapse of the open HCF channels. This work demonstrates a controlled conversion route from Co-HCF to derived oxide, offering a promising pathway for next-generation supercapacitors (SCs) and sustainable energy storage technologies.

Keywords: cobalt hexacyanoferrates, thermal conversion, derived oxides, pseudocapacitor, cyclic voltammetry, kinetics.

1 Introduction

The world is facing an urgent energy crisis due to the rapid depletion of fossil fuels and the ever-growing global energy demand. Over-reliance on fossil fuels has led to serious consequences, such as increased



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carbon dioxide (CO₂) emissions and related hazards like climate change and global warming [1–4]. To overcome these challenges, it is essential to reduce reliance on fossil fuels and shift towards sustainable renewable energy sources such as solar, wind, and hydropower. However, the intermittent nature of these renewable energy sources necessitates the development of efficient energy storage and conversion technologies to provide a reliable power supply for electric vehicles, portable electronic devices, and grid-scale applications [5].

Supercapacitors are electrochemical energy storage devices that have attracted much attention due to their high-power density, fast charge and discharge capabilities, long cycle life, and excellent safety compared to traditional batteries such as fuel cells and lithium-ion batteries [6–14]. SCs fall between traditional capacitors and batteries, making them ideal for applications requiring high-power pulses. Based on their energy storage mechanism, SCs can be classified into three main categories: electric double-layer capacitors (EDLCs), pseudocapacitors, and hybrid supercapacitors. Pseudocapacitors utilize a rapid and reversible faradaic redox process to store energy near the surface of the electrode material [15, 16]. Electric double-layer capacitors (EDLCs) operate based on the separation of non-faradaic charges at the electrode-electrolyte interface. EDLCs offer high specific power density and cycle stability, but relatively low energy density. Pseudocapacitors, on the other hand, combine high energy density, moderate power output, and good cycle durability [17]. The hybrid supercapacitor combines the qualities of pseudocapacitor and EDLC and has better characteristics than individual components [18]. The electrochemical performance of supercapacitors mainly depends on the electrode materials that should possess high surface area, good electrical conductivity, abundant redox activity and structural stability [19–31].

Metal-organic frameworks (MOFs) have been designed as versatile precursors and templates for the derivation of high-performance electrode materials due to their crystalline porous structures with metal nodes connected by organic linkers [32, 33]. These materials possess very high surface areas, tunable pore sizes, flexible chemical compositions, and are thus ideal candidates for gas storage, separation, catalysis, and energy applications. MOFs can be directly used as electrodes or used as sacrificial precursors to synthesize metal oxides [34, 35], sulphides [27],

phosphides or carbon composites [33, 36] with inherited hierarchical porosity and improved conductivity [36]. Their structural flexibility allows for precise engineering of the design of active sites and morphologies, overcoming limitations of traditional materials like agglomeration and poor ion diffusion [37, 38]. Recent advances have demonstrated that MOF-based electrodes can achieve superior specific capacitances, cycling stability and power densities in supercapacitors and batteries, making them the forerunners for next generation energy storage [39, 40].

A unique subclass of MOFs is hexacyanoferrate (HCF), with the general formula $A_xM[M'(CN)_6]_y \cdot nH_2O$, where A represents alkali metal cations and M, M' denote the transition metals. PBAs have a highly open three-dimensional cubic framework with large interstitial channels, high specific surface area, tunable metal compositions and uniform distribution of redox-active sites [41, 42]. These structural features contribute to rapid ion diffusion and efficient mass transport. Furthermore, their low cost, room-temperature synthesis, and morphological diversity (cubes, hollow structures, or polyhedra) are beneficial for energy storage [41, 43]. Upon controlled thermal annealing, cyanide ligands decompose with gas evolution (e.g. CO₂, N₂) and lead to porous metal oxide derivatives with inherited precursor morphology [37, 44]. Cobalt-based hexacyanoferrate (Co-HCF) is especially promising due to the rich redox chemistry of its cobalt centers, fast faradaic charge and discharge, desirable ion mobility, and high porosity; its open framework structure enables rapid electrolyte ion intercalation/de-intercalation [45, 46]. The Co and Fe ions in Co-HCF undergo reversible redox reactions during the charge/discharge process, contributing to pseudocapacitive-like behavior, improved electron transfer, and enhanced overall performance, making them suitable for energy storage devices.

However, the thermal conversion at moderate temperature transforms the cyanide-bridged coordination polymer into spinel Co₃O₄ with optimized Co valence states, high surface area, and improved conductivity [44, 47, 48]. Recent studies on Co-HCF derived Co₃O₄ have reported that this precursor-derived approach often provides shorter diffusion paths, superior rate performance, better-exposed active sites, and good structural buffering during cycling, underscoring the effectiveness of this templating strategy [49, 50]. This thermal conversion involves a trade-off:

although annealing induces the collapse of the framework and formation of porous oxides with potentially improved stability and reduced framework degradation, it may also lead to a decrease in capacitance compared to Co-HCF due to partial loss of the highly open coordination framework structure and reduced accessibility of redox-active sites [49]. Yet, the derived oxides frequently exhibit superior long term stability and mechanical robustness, making them competitive for practical supercapacitor applications [51–53]. Metal-HCFs are promising candidates for electrochemical energy storage owing to their rich redox properties, which render them favorable electrode materials for pseudocapacitors [52].

In the present work, we study the transformation of as-synthesized Co-HCF to nanostructured derived oxide by a thermal treatment at 400 °C. This mild thermal treatment allows controlled framework collapse, complete removal of organic ligands and formation of derived oxide. A comprehensive comparative characterization of both the Co-HCF and derived oxide samples was performed by XRD to track phase transformation from cubic HCF to oxide, FTIR to monitor the disappearance of CN stretching vibrations and formation of Co-O bonds, SEM for surface and morphological evaluation, EDX to investigate the compositional changes with oxygen incorporation and CV for electrochemical evaluation, redox activity and pseudocapacitive performance [31]. The derived oxide sample shows a decrease in capacitance relative to Co-HCF, primarily due to structural densification, but exhibits enhanced cyclic stability [54, 55]. This study provides fundamental insights into the structure-property relationships during the PBA to oxide thermal conversion process, highlights a simple, sustainable route towards high-performance materials, which contributes to the ongoing development of HCF derived oxides as viable candidates for advanced sustainable energy technologies [48, 56–58].

2 Synthesis Procedures and Experimental Details

The synthesis method of Co-HCF was adopted from the reference [29], except by adding 0.2 mL of HCl rather than 0.1 mL into the solution. The obtained Co-HCF powder was annealed in air at 400 °C for 150 min to prepare its derived oxide. This moderate heat treatment condition was chosen to control the decomposition of cyanide ligands, framework collapse and conversion into derived oxide, while maintaining

its overall morphology. The structure, morphology, composition and chemical properties of Co-HCF and its derived oxide were comprehensively analyzed by a variety of physical characterization techniques such as FTIR, XRD, SEM and EDX. XRD was used to study the phase purity and crystallinity of the sample using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). FTIR analysis was used to study the chemical bonds and functional groups in the sample. SEM and EDX were used to evaluate the morphology and elemental composition of the prepared sample. For electrochemical characterization, the electrode was prepared using the conventional method described in references [29, 59]. Briefly, the active material, carbon black, and polyvinylidene fluoride (PVDF) binder were mixed in a mass ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP) solvent. The resulting slurry was coated onto nickel foam current collectors with a typical active material mass loading of approximately $1\text{--}2 \text{ mg cm}^{-2}$ and dried at 60 °C for 12 h before electrochemical testing. After preparation, the sample was characterized and finally tested as an electrode material for asymmetric supercapacitors on a potentiometer (Gamry Instruments 1000E). The working electrode in the three-electrode system is the Co-HCF or derived oxide sample, the reference electrode is $\text{Hg/Hg}_2\text{Cl}_2$, and the counter electrode is a platinum (Pt) wire.

3 Results and Discussion

3.1 Structural and Morphological Characterizations

The structural, elemental, chemical and morphological properties of Co-HCF and its derived oxide were comprehensively investigated using XRD, FTIR, SEM and EDX spectroscopy [53, 60]. The XRD pattern of Co-HCF, shown in Figure 1(a), displays sharp diffraction peaks that match well with the standard JCPDS card no. 00-024-0327. Prominent peaks appeared in the 2θ range of 15° to 60° . The calculated lattice parameter of $10.3 \text{ \AA}$ is in excellent agreement with the standard value of approximately $10.2\text{--}10.3 \text{ \AA}$ reported in the same card for $\text{Co}_3[\text{Fe}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$. This close match confirms the successful formation of Co-HCF with high crystallinity, phase purity and structural integrity, consistent with the FCC cubic framework characteristic of metal hexacyanoferrate. The average crystallite size, calculated using the Williamson–Hall plot, was found to be 31.3 nm , and the microstrain was 5.7×10^{-4} . The open cubic structure with large interstitial channels is characteristic of HCF and efficient for ion diffusion in electrochemical

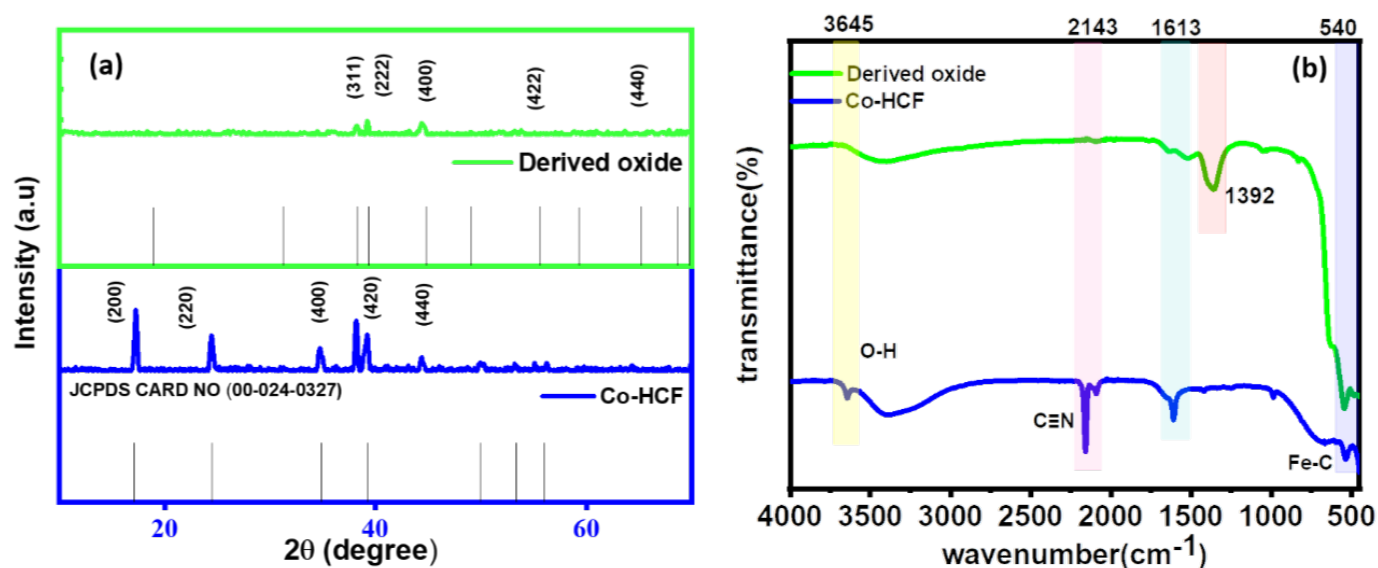


Figure 1. (a) XRD patterns, (b) FTIR spectra of Co-HCF and derived oxide.

applications [47, 49]. Nevertheless, in the XRD pattern of derived oxide, the characteristic HCF peaks disappear, and new diffraction peaks are observed in the 2θ range of 15° to 70° , indicating the spinel cubic phase of Co_3O_4 . The peaks observed in the derived oxide do not follow the original HCF trend due to the collapse of the cyanide-bridged framework and formation of a dense spinel oxide structure. The crystallite size of derived Co_3O_4 slightly increases due to thermal treatment but remains in the nanoscale regime [29, 61, 62].

FTIR spectroscopy further confirmed the structural assessment of Co-HCF and derived oxide. The broad absorption peak observed around $3200\text{--}3644\text{ cm}^{-1}$ was associated with the O–H stretching vibrations, indicating the presence of adsorbed water and coordinated water molecules in the HCF framework [63]. The spectrum of Co-HCF, shown in Figure 1(b), displays a strong characteristic absorption band near $2090\text{--}2170\text{ cm}^{-1}$, attributed to the $\text{C}\equiv\text{N}$ stretching vibrations of the cyanide ligands ($\text{Co}^{3+}\text{--CN--Co}^{2+}$ and related modes) [64, 65]. Other absorption bands near $1600\text{--}1650\text{ cm}^{-1}$ were associated with the bending vibrations of coordinated water and interstitial water molecules present in the HCF framework [59, 65]. The bending vibrations of metal-carbon (Fe–C) and cobalt-nitrogen (Co–N) bonds occur in the low frequency region at 600 and 505 cm^{-1} respectively [62, 64]. In derived oxide, the intense CN stretching bands completely disappear during annealing, confirming the successful removal of the cyanide groups through thermal decomposition. The bands emerging in the $550\text{--}670\text{ cm}^{-1}$ region

are assigned to Co–O stretching vibrations of the Co_3O_4 lattice, confirming the conversion of the HCF framework into the derived oxide. The reduction of water-related bands indicates dehydration during thermal treatment [65].

SEM images reveal the morphological features of both samples, as shown in Figure 2(a, c). The Co-HCF exhibits well defined cubic morphology with relatively smooth surfaces, consistent with typical HCF morphologies obtained via co-precipitation [59]. After annealing the overall cubic morphology is mainly preserved, but the surface becomes rougher and more porous due to gas evolution during cyanide group decomposition. No severe agglomeration of the overall structure occurs at this optimized temperature [66, 67].

EDX analysis in Figure 2(b,d) confirms the elemental composition of the prepared samples. The Co-HCF spectrum shows the presence of cobalt (Co), carbon (C), oxygen (O), nitrogen (N) and minor potassium (K) from the precursor, with relatively the same expected ratios supporting the HCF framework. In the annealed sample, the carbon and nitrogen peaks significantly decrease, while the oxygen peak increases substantially [68], consistent with the formation of the derived oxide [62].

3.2 Electrochemical Performance

The electrochemical performance of as-synthesized Co-HCF and derived oxide was thoroughly evaluated using CV in a three-electrode configuration with 3 M KOH electrolyte. The Co-HCF and derived oxide were pasted on nickel foam and tested under identical

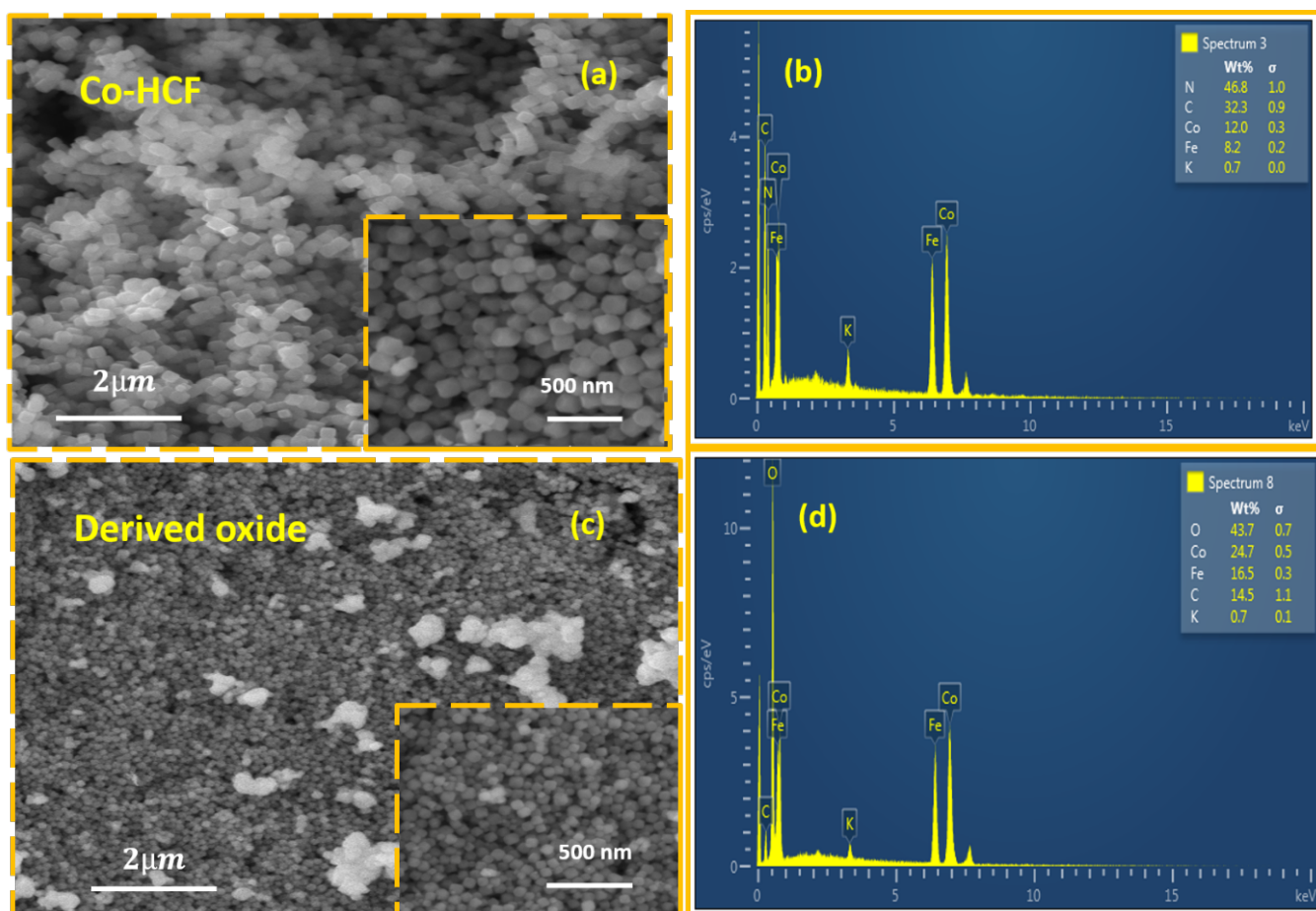


Figure 2. (a, c) FESEM images, (b, d) EDX spectra of Co-HCF and derived oxide.

conditions to enable direct comparison of the effect of thermal conversion on pseudocapacitive behavior.

Typically, CV curves of Co-HCF (Figure 3(a)) exhibit a pair of well-defined redox peaks within a potential window of 0.6 to 1.0 V, characteristic of Faradaic redox reactions associated with the reversible conversion between $\text{Co}^{2+}/\text{Co}^{3+}$ oxidation states in the open HCF framework. CV measurements were performed at scan rates ranging from 5 to 100 mV s^{-1} , and the well-retained redox peak shapes indicate good rate capability and fast ion diffusion through the large interstitial channels of the cubic HCF structure. The specific capacitance calculated from CV curves, shown in Figure 3(b), reached a maximum value of 624 F g^{-1} at 5 mV s^{-1} for Co-HCF, demonstrating excellent pseudocapacitive performance. In contrast, as shown in Figure 3(c), the derived oxide shows redox peaks corresponding to the Co_3O_4 spinel phase but with slightly shifted peak positions and reduced peak currents [62]. The specific capacitance of the derived oxide, as shown in Figure 3(d), decreased to 143 F g^{-1} at the same scan rate. This reduction is attributed to the partial collapse of the highly open cyanide-linked

framework during thermal treatment, decreasing the number of readily accessible redox-active sites and ion intercalation channels despite the formation of a porous structure. Nevertheless, the CV curves of derived oxide maintain better symmetry and less distortion at high scan rates, which suggests improved reversibility [60, 69].

To better understand the charge storage mechanism, the CV curves were further investigated by the Randles–Ševčík and Dunn methods to study the charge storage behavior and reaction kinetics of both samples. The value of b provides insights into the nature of the charge storage process and was analyzed using the power law relationship $I_{pc} = av^b$, where I_{pc} is the peak current and v is the scan rate: a b value closer to 0.5 indicates a diffusion-controlled process, while a value near 1 signifies surface-controlled capacitive behavior [70, 71]. Figure 4(a) shows the fitting of the logarithm of peak currents (I_{pc}) versus the logarithm of scan rate (v) to obtain the b -values. The fitted b -values for Co-HCF and the derived oxide were determined to be 0.99 and 0.97, respectively. This demonstrates that the electrochemical response

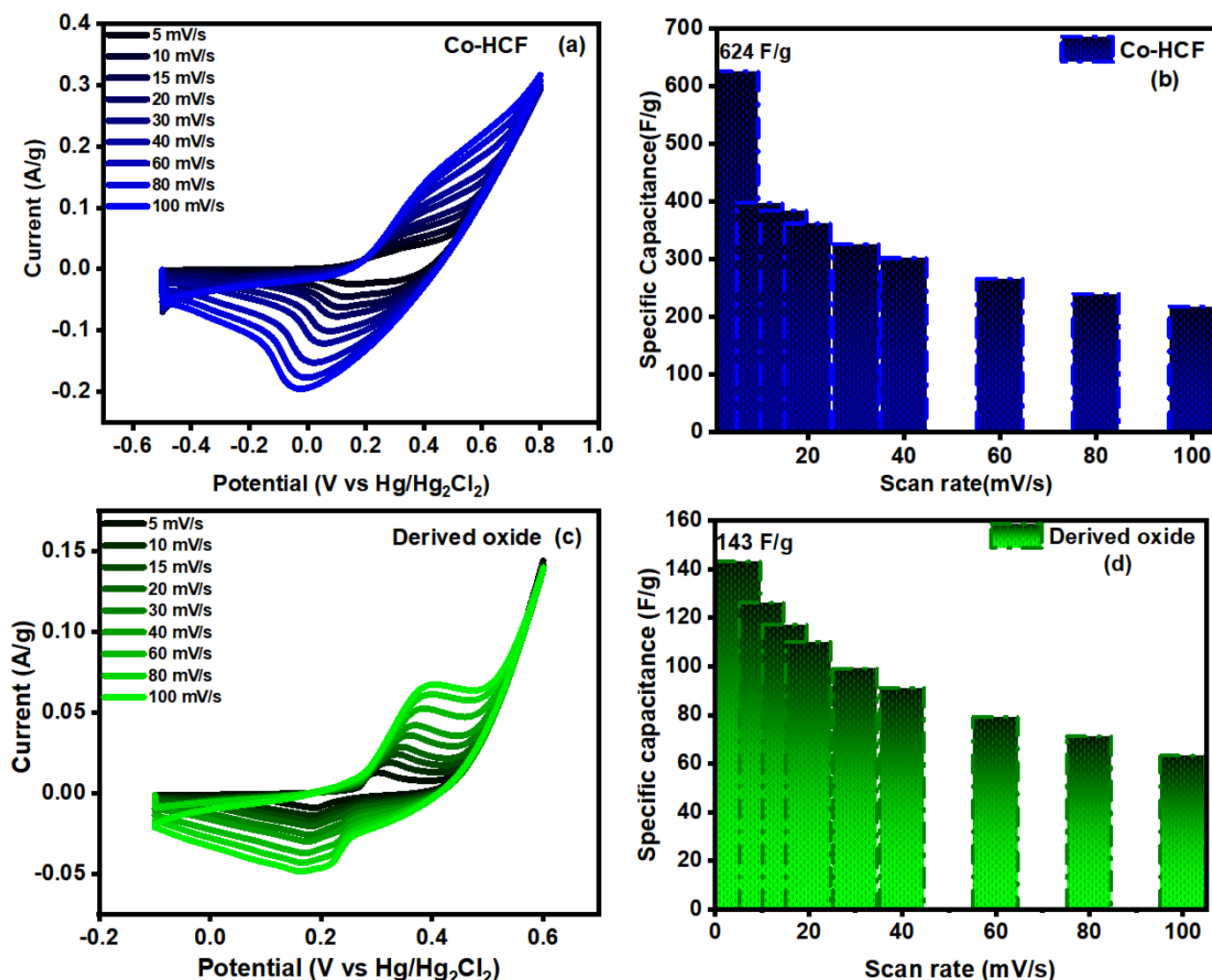


Figure 3. (a, c) CV curves at various scan rates, (b, d) C_s vs. ν plots of Co-HCF and derived oxide.

in both samples is dominated by surface-controlled pseudocapacitive process, which is highly desirable for supercapacitor applications as it enables fast charge/discharge and high rate capability. The slightly higher b value for Co-HCF underscores its more ideal capacitive characteristics, consistent with its higher specific capacitance, while the derived oxide still exhibits pseudocapacitive behavior with improved cyclic stability. This power-law kinetic analysis has been widely employed to distinguish capacitive from diffusion-controlled processes in pseudocapacitive electrode systems [70, 72]. Figure 4(b) plots the peak current/square root of scan rate ($I_p/\nu^{1/2}$) vs. the square root of scan rate ($\nu^{1/2}$), showing a strong linear relationship with a relatively good fitting parameter. Furthermore, the diffusive and capacitive contributions were calculated using Dunn's method as shown in Figure 4(c). It reveals that Co-HCF exhibits a dominant diffusion-controlled contribution

(98%) at 20 mV/s, indicating that intercalation-type faradaic processes play a major role in charge storage through the open channels of the HCF framework. The annealed sample (Figure 4(d)) shows a slightly reduced diffusion-controlled contribution (91%) at the same scan rate, suggesting a modest increase in the surface capacitive fraction following thermal conversion. Taken together, the high b -values (0.99 and 0.97) and the dominant diffusion-controlled contributions indicate that the charge storage in both samples is governed by intercalation-type pseudocapacitive processes, which are fast and reversible due to the open framework and abundant redox-active cobalt centers [60, 70].

4 Conclusions

In summary, the Co-HCF was successfully synthesized via a simple and cost-effective co-precipitation method.

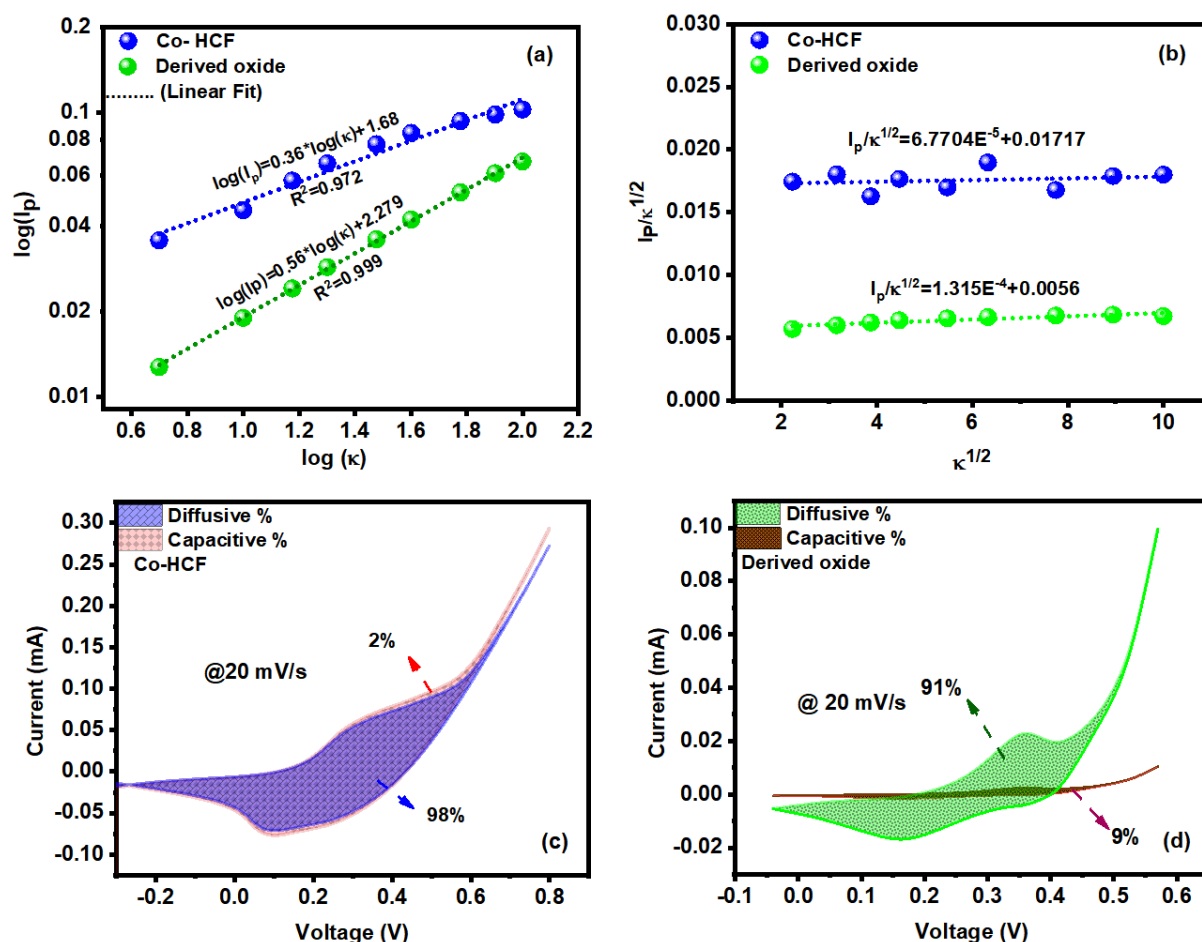


Figure 4. (a) slope of $\log I_{pc}$ vs. v to calculate 'b' values, (b) slope line between $I_{pc}/v^{1/2}$ vs. $v^{1/2}$, (c, d) capacitive and diffusive contribution at 20 mV/s of Co-HCF and derived oxide.

The prepared Co-HCF was annealed in air at 400 °C for 150 min to further transform it into a derived oxide. Physicochemical characterization using XRD, FTIR, SEM, and EDX confirmed the complete transformation of the Co-HCF framework into derived oxide. The annealing process thoroughly removed the cyanide ligands, resulting in favorable porosity while maintaining the overall cubic morphology and increasing surface roughness. Electrochemical studies in KOH electrolyte showed that the synthesized Co-HCF electrode exhibited excellent pseudocapacitive performance. Its open three-dimensional framework and abundant redox-active cobalt sites promoted rapid ion diffusion and Faradaic reactions, achieving an excellent specific capacitance of 624 F g^{-1} at a scan rate of 5 mV s^{-1} . The derived oxide electrode after thermal conversion exhibited a lower specific capacitance of approximately 143 F g^{-1} under the same conditions. The reduction is primarily attributable to the partial collapse of the highly open HCF structure and lower accessibility of the redox sites. However, the derived oxide showed

significantly enhanced cycling stability and improved electrochemical reversibility than the Co-HCF owing to the robust Co_3O_4 phase and improved structural integrity. The present study highlights the trade-off between high initial capacitance of the precursor Co-HCF and the excellent long-term stability of derived oxide. This controllable thermal conversion strategy provides a facile and scalable approach to design stable earth-abundant pseudocapacitive materials for supercapacitor applications. The results provide fundamental insights into the structure-property relationships during the HCF to metal oxide transformation and show the potential of HCF-derived oxides as promising electrode materials for the next generation of sustainable energy storage devices. Further optimization of the annealing conditions or incorporation of conductive additives and composite architectures represents a promising avenue for future work aimed at enhancing the capacitance of the derived oxide while retaining its excellent long-term stability.

Data Availability Statement

Data will be made available on request.

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Conflicts of Interest

The authors declare no conflicts of interest.

AI Use Statement

The authors declare that no generative AI was used in the preparation of this manuscript.

Ethical Approval and Consent to Participate

Not applicable.

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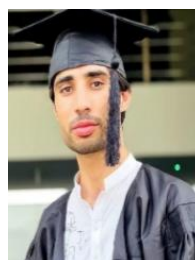
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