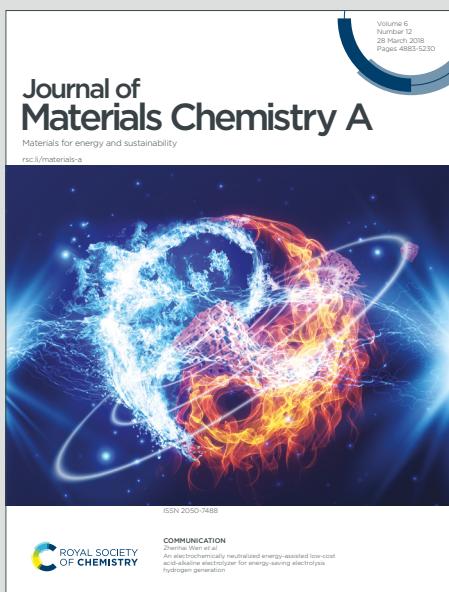


# Journal of Materials Chemistry A

Materials for energy and sustainability

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**Additive Free Co-Lean Ternary NiCoAl/Ni Foam Electrode for High-Efficiency Energy Storage and Low-Grade Heat Harvesting**View Article Online  
DOI: 10.1039/CA08297HP. Rupa Ranjani <sup>a, b, c</sup>, Anjali Ashokan <sup>b</sup>, Subhajit Biswas <sup>b, c</sup>, Justin D. Holmes <sup>b, c</sup> and Kafil M. Razeeb <sup>a\*</sup><sup>a</sup> *Micro-Nano System Centre, Tyndall National Institute, Cork T12 R5CP, Ireland.*<sup>b</sup> *School of Chemistry, University College Cork, Cork T12 YN60, Ireland.*<sup>c</sup> *Environmental Research Institute, University College Cork, Cork, T23 XE10, Ireland.**Corresponding authors:* [kafil.mahmood@tyndall.ie](mailto:kafil.mahmood@tyndall.ie)**Abstract**

This work aims to develop a sustainable, additive-free, and Co-lean ternary NiCoAl layered double hydroxide (NCA) electrode capable of delivering high-performance electrochemical energy storage and low-grade heat harvesting. A Ni-rich, Co-lean NCA was directly grown on nickel foam (NCA/NF) via a simple hydrothermal process, forming 3D hierarchical microflowers composed of ultrathin (27 nm) nanosheets. The optimized Ni:Co:Al ratio (4:2:1) maximizes  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox activity, stabilizes the LDH lattice through  $\text{Al}^{3+}$  incorporation, and enhances charge-transfer kinetics via Ni-O-Co interactions. The resulting NCA/NF electrode delivers a specific capacitance of 3346 F g<sup>-1</sup> (5019 mF cm<sup>-2</sup>) at 1.5 A g<sup>-1</sup> and enables an asymmetric supercapacitor with a specific energy of 55.4 Wh kg<sup>-1</sup> at 797.7 W kg<sup>-1</sup>, retaining 51.1 Wh kg<sup>-1</sup> even at 7998.2 W kg<sup>-1</sup>. Combined with 92% capacity retention over 25,000 cycles, the NCA/NF electrode simultaneously retains specific energy and power capability. This well-balanced energy-power-stability performance is a critical requirement for next-generation high-power electrochemical systems and is rarely achieved in fully additive-free LDH electrodes. In parallel, the NCA/NF electrode functions as an efficient thermoelectrochemical material, achieving a Seebeck coefficient of 5.5 mV K<sup>-1</sup> and storing 1.65 J of thermal charge under a modest 0-10 K gradient. This performance has not previously been reported for Ni-based electrodes at such low  $\Delta T$ . These findings establish Ni-rich, Co-lean NCA/NF as a scalable and sustainable bifunctional electrode platform that unites compositional tuning, structural integrity, and efficient energy storage and conversion capability.

**Keywords:** Nickel cobalt aluminium layered double hydroxide (NiCoAl LDH), Co-lean Ni-rich composition, Asymmetric supercapacitor, Thermoelectrochemical cell, Bifunctional electrode, energy storage and conversion

## 1. Introduction

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The rapid depletion of fossil fuels and the escalating impacts of climate change have created an urgent demand for sustainable energy technologies<sup>1</sup>. While rechargeable batteries dominate large-scale storage, their relatively slow charge/discharge rates, finite cycling lifetimes, and safety concerns have stimulated interest in complementary systems<sup>2</sup>. Supercapacitors, offering high power density, and thermoelectrochemical cell (TEC), enabling direct heat-to-electricity conversion, are emerging as sustainable energy technologies<sup>3,4</sup>. In both systems, electrode materials play a decisive role in determining the overall performance of the device, influencing parameters such as charge storage capacity, energy conversion efficiency, power output, and durability.

A wide range of electrode materials including carbon frameworks, MXenes, MOFs, COFs, and transition-metal oxides<sup>4-8</sup> have been investigated, but despite their attractive features, many suffer from limited capacitance, poor structural stability, low Seebeck coefficient or complex, high-temperature multi-step synthesis<sup>2</sup>. In recent years, transition metal-based layered double hydroxides (LDHs) have attracted significant attention. They can be prepared through simple, low-temperature, one-step processes with minimal chemical input. Moreover, LDHs offer abundant redox-active sites and tunable layered structures, making them highly versatile for electrochemical energy storage applications<sup>5,6</sup>. LDHs, commonly described by the general formula  $[M^{II}_{1-x} M^{III}_x (OH)_2]^{x+} [A_{x/n}^{n-}]^{x-} \cdot mH_2O$  where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent metal cations, and  $A^{n-}$  is a charge-balancing anion such (e.g.  $CO_3^{2-}$  or  $NO_3^-$ )<sup>7</sup>. Their structure consists of positively charged hydroxide layers separated by interlayer anions and water molecules. This compositional flexibility has driven widespread interest in LDHs for various energy applications.

Binary and ternary systems such as CoFe, CoMn, NiCoFe, NiCoMn, and NiCoCu<sup>8,9</sup> have demonstrated enhanced electrochemical activity, but LDHs still face persistent challenges including low intrinsic conductivity, nanosheet restacking, and phase segregation, often necessitating conductive scaffolds to retain performance. While cobalt incorporation improves conductivity and redox activity, its toxicity, scarcity, and ethically problematic extraction raise significant sustainability concerns, highlighting the need for Ni-rich, Co-lean alternatives that maintain electrochemical performance while advancing environmental responsibility<sup>10</sup>. Among ternary LDHs, NiCoAl has emerged as a particularly effective system, coupling Ni-centered redox activity with reduced Co-mediated conductivity and  $Al^{3+}$ -induced lattice stabilization<sup>11</sup>. Optimized Ni:Co:Al ratios enhance crystallinity, hydrophilicity, and nanosheet

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stacking compared with other trivalent substitutions (e.g.  $Mn^{3+}$ ,  $Fe^{3+}$ ,  $Ti^{3+}$ ), yielding ternary LDHs with charge-storage kinetics and conductivity that frequently surpass binary analogues such as  $NiAl$ ,  $CoAl$ , or  $NiMn$ <sup>8</sup>.

The hydrothermal route offers a versatile and controllable synthetic strategy, allowing precise regulation of nucleation and crystal growth under mild conditions<sup>12</sup>. Among its variants, one-pot hydrothermal synthesis is particularly advantageous due to its simplicity, scalability, and ability to directly deposit LDHs onto conductive substrates (e.g., nickel foam, carbon cloth, titanium mesh) without the need for binders or additives<sup>13</sup>. Despite these advantages, ultrathin LDH nanosheets synthesized by one-pot methods often tend to self-aggregate, which reduces electrolyte penetration and slows ion diffusion, thereby limiting charge-storage kinetics. To overcome this, the formation of three-dimensional (3D) hierarchical microflower architectures from interconnected nanosheets has emerged as an effective design. Compared with coral<sup>14</sup>, spindle<sup>15</sup> or spherical morphologies<sup>16</sup>, the microflower structure provides a high surface area, abundant exposed redox-active sites, and interconnected ion/electron pathways, significantly enhancing electrochemical performance<sup>12,17</sup>. In situ growth of LDH microflowers on conductive substrates such as Ni foam (NF) establishes a coherent interface that minimizes charge-transfer resistance and enhances structural integrity. The binder-free configuration promotes efficient ion-electron transport, delivering superior rate performance and cycling stability relative to conventional layered morphologies<sup>13</sup>.

Electrochemical studies of trimetallic LDHs, particularly NiCoAl (NCA) systems, have demonstrated high specific capacitance and energy density arising from the synergistic roles of Ni redox activity, Co-assisted conductivity, and  $Al^{3+}$  stabilization<sup>18</sup>. For instance,  $NiCo_2Al$  LDH electrode delivered a capacitance of  $2369\text{ F g}^{-1}$  at  $1\text{ A g}^{-1}$  and energy density of  $91\text{ Wh kg}^{-1}$  in asymmetric supercapacitor<sup>19</sup>. However, such high performance is typically associated with Co-rich compositions, highlighting the need for Ni-rich, Co-lean alternatives that can achieve comparable or superior results while enhancing sustainability.

Beyond conventional supercapacitors, NCA LDHs exhibits significant potential in TEC. Conventional thermoelectric generators are limited by low Seebeck coefficients ( $100\text{--}800\text{ }\mu\text{V K}^{-1}$ )<sup>20</sup> and dependence on scarce or toxic elements such as Pb and Te. Recently, TEC have leveraged ionic thermodiffusion and redox thermogalvanic effects to achieve Seebeck coefficients several orders of magnitude higher than those of conventional solid-state systems. While liquid redox couples have traditionally been used, they can suffer side reactions (e.g.

hydrogen evolution) at high temperatures or extreme pH, limiting stability. An emerging electrode-centric approach employing solid redox-active electrodes in alkaline electrolytes avoids these issues.

Based on our previous report<sup>21</sup>,  $\text{NiSe}_2/\text{CoSe}_2$  electrodes directly grown on carbon cloth achieving a Seebeck coefficient of  $-3.4 \text{ mV K}^{-1}$  in 1 M NaOH, this work advances toward NCA LDHs to further enhance thermoelectric performance while ensuring material sustainability. With multivalent redox centers, hydrophilic layered frameworks, and tuneable 3D morphologies, NCA LDHs provide a compelling platform to act as a bifunctional electrode towards high-performance supercapacitors and thermoelectrochemical cells<sup>22</sup>. To address these challenges, a facile *in situ* growth of binder and additive-free LDH architectures on conductive scaffolds, coupled with compositional tuning toward Ni-rich, Co-lean phases, is essential to promote sustainability, superior charge-storage and energy-conversion efficiency.

Here, Co-lean  $\text{Ni}_{0.57}\text{Co}_{0.28}\text{Al}_{0.14}$  LDH is demonstrated for the first time as a bifunctional electrode for both assymetric supercapacitor (ASC) and TEC. A 3D hierarchical microflower architecture with a Ni: Co: Al ratio of 4:2:1 was directly grown on NF through one-step hydrothermal route, without binders, dopants, or conductive additives, ensuring coherent substrate integration and structural robustness. In this composition, cobalt is deliberately maintained at a substantially lower level than nickel and reduced relative to the Co-rich NiCoAl LDHs commonly reported in the literature<sup>18,19</sup>, while  $\text{Al}^{3+}$  is incorporated in a controlled amount to stabilize the layered framework. The hierarchical nanosheet assembly, abundant surface functionalities, and stabilized mixed-valence states facilitate efficient charge transport and reversible redox kinetics. The rational integration of Ni, Co, and Al in a Co-lean ternary LDH yields an additive-free, bifunctional electrode uniting sustainable composition, scalable synthesis, and dual electrochemical-thermoelectrochemical performance.

Although LDHs and hydrothermal growth strategies are widely reported for electrochemical energy storage<sup>23–26</sup>, most LDH electrodes are optimised for a targeted electrochemical application and commonly rely on conductive additives<sup>27,28</sup> or composite architectures<sup>29</sup> to preserve structural integrity and electrochemical stability. Here, an additive-free, Ni-rich and Co-lean NCA/NF LDH is engineered via compositional and structural tuning to stabilise the  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox process and support both capacitive charge storage and thermal energy conversion. By reducing cobalt content and incorporating  $\text{Al}^{3+}$  as a structural stabilising species, the LDH phase is driven towards a Ni-dominated and highly reversible  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox

pathway that maintains mechanical robustness and electronic continuity without external conductive additives.

When NCA/NF is employed as a positive electrode in an asymmetric supercapacitor within a commercial PAT cell, the device delivered ultrahigh energy and power density, high-rate capability, and long-term durability. In a symmetric thermoelectrochemical cell it simultaneously exploited entropy-driven Ni/Co redox transitions to harvest low-grade heat, achieving a Seebeck coefficient of  $5.5 \text{ mV K}^{-1}$  under an ultralow temperature gradient of 0-10 K with thermal charge storage of 1.65 J. These results establish a materials design strategy based on binder-free compositional tuning that yields a stable redox-active electrode architecture. The demonstrated synergy of Ni-Co-Al chemistry, oxygen-mediated redox activity, and hierarchical architecture broadens the functional scope of LDH-based materials, advancing a sustainable route towards next-generation cobalt-lean energy storage and conversion systems.

## 2. Experimental

### 2.1. Materials

All reagents were of analytical grade and used as received without further purification. Nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), Cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), Aluminium nitrate nanohydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), Ammonium fluoride ( $\text{NH}_4\text{F}$ ), and Urea ( $\text{CH}_4\text{N}_2\text{O}$ ) were purchased from Sigma-Aldrich (Ireland). Additionally, commercial NF (99% Ni, 1 mm thickness and 80-120 pores per inch (PPI)), was obtained from Fuel Cell Store (USA). All aqueous solutions were prepared with deionised (DI) water. Prior to synthesis, NF substrates ( $1 \times 1 \text{ cm}^2$ ) were cleaned by immersion in 3 M HCl for 15 min, followed by rinsing with ethanol and DI water to remove surface impurities.

#### 2.1.1. Hydrothermal synthesis of In-situ grown NiCoAl LDH on Ni foam.

To initially evaluate the influence of cation stoichiometry on phase formation and morphology, a series of Ni-Co-Al LDHs were hydrothermally grown on NF by varying only the Al precursor concentration while maintaining a constant Ni:Co ratio. Increasing the Al content (e.g., precursor ratios 4:2:6 and 4:2:3) produced disordered, thickened, and irregular platelet structures, indicating that excessive Al disrupts the nucleation and lateral growth required for well-defined LDH nanosheets (Fig. S1). In contrast, lower Al incorporation promotes the development of thin, vertically aligned nanosheets that assemble into uniform microflower

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architectures, which is consistent with the previous reports<sup>11,36–38</sup>. These trends demonstrate

that precise tuning of the Al content governs nanosheet thickness, stacking behaviour, and hierarchical organisation. Notably, the 4:2:1 composition provides an optimal Al level that yields the most structurally coherent and functionally advantageous microflower morphology, characterised by highly ordered, interconnected hexagonal nanosheets.

Guided by this optimisation, the in-situ Co-lean NCA LDH was grown on NF was synthesised through a facile one-pot hydrothermal synthesis (Scheme S1). In a typical procedure,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.2 M),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.1 M), and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.05 M) were dissolved in 80 mL of DI water to obtain a clear solution with a Ni:Co:Al molar ratio of 4:2:1. Ammonium fluoride ( $\text{NH}_4\text{F}$ , 0.1 g) and urea ( $\text{CH}_4\text{N}_2\text{O}$ , 0.3 g) were then added under magnetic stirring for 15 min (at 60°C) to ensure homogeneity. The precursor solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave containing a pretreated NF substrate, sealed and maintained at 150 °C for 15 h. After natural cooling to room temperature, the samples were rinsed thoroughly with acetone, DI water (3 times), and dried at ambient conditions to yield NCA/NF. For comparison, binary  $\text{Ni}_{0.8}\text{Al}_{0.2}/\text{NF}$  (NA/NF) and  $\text{Co}_{0.67}\text{Al}_{0.33}/\text{NF}$  (CA/NF) electrodes were synthesised under identical conditions using Ni: Al and Co: Al molar ratios of 4:1 and 2:1, respectively.

## 2.2. Structural and surface characterisation

Comprehensive physical characterisation was conducted on NCA/NF, NA/NF, and CA/NF. Phase purity was examined by X-ray diffraction (XRD, PANalytical X'Pert PRO, Cu  $\text{K}\alpha$ ,  $\lambda = 0.15406$  nm). Functional groups and lattice vibrations were analysed using Fourier-transform infrared spectroscopy (FT-IR, PerkinElmer) and Raman spectroscopy (Renishaw RA100, 514.5 nm). Morphology and elemental composition were studied by field emission scanning electron microscopy (FE-SEM, FEI QUANTA 650) with energy-dispersive X-ray spectroscopy (EDX, Oxford INCA), and microstructural features by high-resolution transmission electron microscopy (HRTEM, JEOL 2100, 200 kV), with samples detached from nickel foam by sonication. Surface chemistry and oxidation states were probed by X-ray photoelectron spectroscopy (XPS, Kratos Ultra DLD, Al  $\text{K}\alpha$ ), while specific surface area and pore size distribution were obtained from nitrogen adsorption/desorption isotherms (Gemini VII 2390) using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner Alenda (BJH) methods.

### 2.3. Electrochemical Measurements

#### 2.3.1. Supercapacitor application

Electrochemical tests, including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS), were performed on a VMP3 Biologic workstation. A three-electrode configuration was employed, in which the as-fabricated LDH/NF electrodes (NA/NF, CA/NF, and NCA/NF;  $1 \times 1 \text{ cm}^2$ ) served as the working electrode, with a total active material loading of  $1.5 \text{ mg cm}^{-2}$ , a platinum wire (99.99% Pt, 0.5 mm diameter) as counter electrode, and a Hg/HgO (+0.098 V vs. SHE at 25 °C) as reference electrode immersed in 1 M KOH electrolyte. An asymmetric supercapacitor (ASC) was assembled in a commercial PAT-Core Cell<sup>39,40</sup> using NCA/NF as the positive electrode ( $1.5 \text{ mg cm}^{-2}$ ), AC/NF (prepared with 80 wt% activated carbon (AC), 10 wt% acetylene black, and 10 wt% PTFE) as the negative electrode ( $1 \times 1 \text{ cm}^2$ ,  $2.5 \text{ mg cm}^{-2}$ ), total active mass is 0.0040 g for ASC device, and a Whatman glass fibre membrane (GFM) infiltrated in 1 M KOH electrolyte as separator. All electrochemical calculation details are provided in the SI (Section 1.1).

#### 2.3.2. Thermoelectrochemical cell (TEC) measurements

TEC studies were carried out using LDH/NF electrodes ( $1 \times 1 \text{ cm}^2$  geometric area) with a total active mass loading of  $1.5 \text{ mg cm}^{-2}$ , operated in 1 M KOH under both isothermal and non-isothermal conditions. In isothermal measurements, three-electrode configuration was employed in 1 M KOH electrolyte with symmetric LDH/NF electrodes as working and counter, and Ag/AgCl as reference. The electrolyte temperature was varied from 20–70 °C, while monitoring the open-circuit potential (E) to calculate the temperature coefficient (TC). While the non-isothermal analysis was evaluated in a transverse TEC setup using symmetric LDH electrodes mounted on Peltier heater and cooler elements connected to a Keithley DC power supply to establish a controlled temperature gradient ( $\Delta T = 0\text{--}10 \text{ K}$ ). Thermocouples were attached to each electrode to measure the temperature difference ( $T_1\text{--}T_2$ ) and a GFM separator ( $1 \times 3 \text{ cm}^2$ ) infiltrated in 1 M KOH (500  $\mu\text{l}$ ) ensured ionic conduction. The open-circuit voltage (OCV) was recorded using a digital multimeter as a function of  $\Delta T$  to determine the ionic Seebeck coefficient ( $S_e$ ) and thermal charge storage ( $J$ ). The corresponding thermoelectrochemical calculation procedures are described in the SI (Section 1.2).

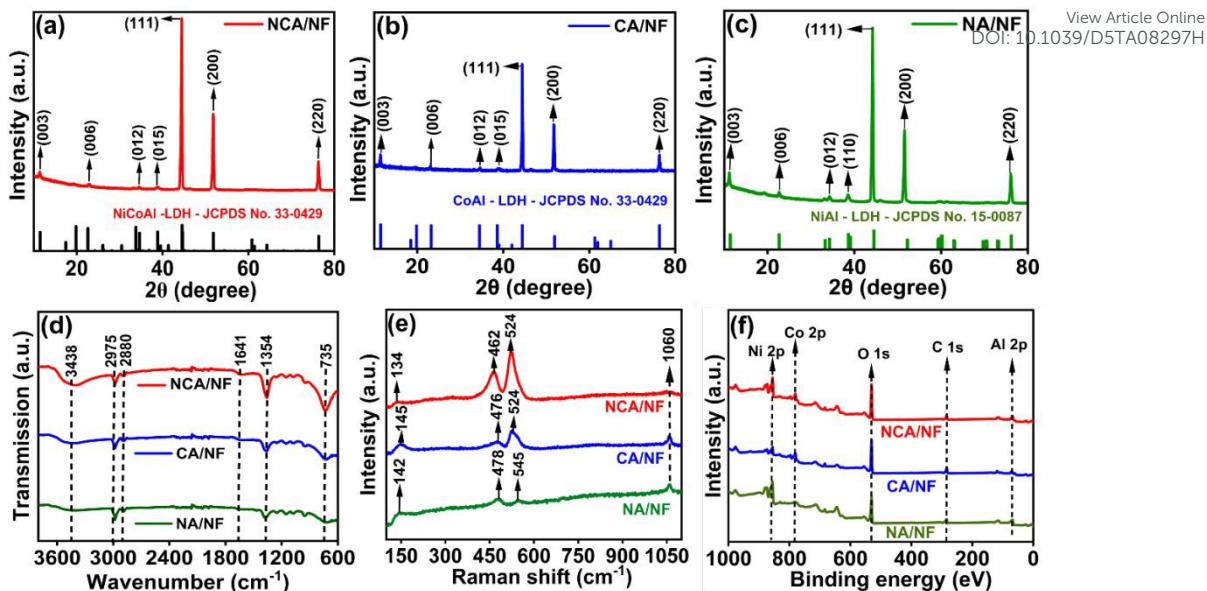
Notably, the LDH/NF electrodes ( $1 \times 1 \text{ cm}^2$ ,  $1.5 \text{ mg cm}^{-2}$ ) and electrolyte conditions (1 M KOH) employed here are identical to those used in the corresponding supercapacitor studies. The use of a consistent electrode architecture and ionic environment across both measurements underscores the intrinsic bifunctional behaviour of the LDH/NF system in thermoelectrochemical energy conversion and electrochemical energy storage.

### 3. Results and Discussions

#### 3.1. Structural, Physical and Chemical Characterization

The XRD pattern of Ni foam (NF) shows (Fig 1a-c) characteristic peaks at  $44.4^\circ$ ,  $51.8^\circ$ , and  $76.3^\circ$ , corresponding to (111), (200), and (220) planes (JCPDS No. 04-0850)<sup>41</sup>. For NCA/NF (Fig. 1a), additional peaks at  $11.4^\circ$ ,  $22.8^\circ$ ,  $34.5^\circ$ , and  $38.8^\circ$  match the (003), (006), (012), and (015) planes of hydrotalcite-like LDH, confirming its crystalline formation<sup>42</sup>. The NA/NF pattern (Fig. 1b) shows reflections at  $11.4^\circ$ ,  $22.8^\circ$ , and  $34.4^\circ$  (JCPDS No. 15-0087), along with  $33.2^\circ$  peak from  $\alpha\text{-Ni(OH)}_2\cdot\text{H}_2\text{O}$  (JCPDS No. 22-0444)<sup>42</sup>. For CA/NF (Fig. 1c), besides substrate peaks, reflections at  $11.4^\circ$ ,  $22.8^\circ$ ,  $34.5^\circ$ , and  $38.8^\circ$  are indexed to nickel cobalt carbonate hydroxide hydrate (JCPDS No. 33-0429)<sup>42</sup>.

FTIR spectra (Fig. 1d) of NCA/NF, NA/NF, and CA/NF show broad O-H stretching ( $3438 \text{ cm}^{-1}$ ) and H-O-H bending ( $1641 \text{ cm}^{-1}$ ) modes from interlayer water and hydroxyl groups<sup>42</sup>. A sharp band at  $1354 \text{ cm}^{-1}$  from  $\text{CO}_3^{2-}$  species, and  $735 \text{ cm}^{-1}$  assigned to M-O lattice vibrations (M = Ni, Co, Al)<sup>43</sup>. Weak absorptions at  $2975$  and  $2880 \text{ cm}^{-1}$  correspond to C-O/C-H stretching, arising from residual organics in NCA/NF and consistent with hydrotalcite-type interlayers in NA/NF and CA/NF. Their low intensity indicates only minor surface contributions, without affecting the layered structural integrity. Raman spectra (Fig. 1e) of NCA/NF, NA/NF, and CA/NF confirm the LDH framework, showing characteristic  $\text{A}_{1g}$  modes at  $462\text{-}478 \text{ cm}^{-1}$  (Ni-OH vibrations) and  $\text{F}_{2g}$  mode at  $524\text{-}545 \text{ cm}^{-1}$  from  $\text{D}_{3h}$  symmetric O-M-O linkages (M = Ni, Co, Al)<sup>44</sup>. Low-frequency lattice modes appear near  $134\text{-}145 \text{ cm}^{-1}$  (metal oxygen vibrations), while a band at  $1060 \text{ cm}^{-1}$  (carbonate band) corresponds to interlayer  $\text{CO}_3^{2-}$  ions<sup>45</sup>.



**Fig. 1** XRD patterns of (a) NCA/NF, (b) CA/NF, (c) NA/NF; (d) FTIR spectra, (e) Raman analysis, (f) XPS survey spectra LDH/NF electrodes.

XPS analysis (Fig. 1f) confirms the surface composition and chemical states of NCA/NF, NA/NF, and CA/NF. The Ni 2p spectra in Fig. S2a in the Supplementary Information (SI) show  $\text{Ni}^{2+}/\text{Ni}^{3+}$  species with doublets at 855.8 eV ( $2p_{3/2}$ ) and 873.3 eV ( $2p_{1/2}$ ), along with shake-up satellites at 861.9 and 879.8 eV, characteristic of  $\text{Ni}(\text{OH})_2$  and  $\text{Ni}^{3+}$  contributions<sup>46</sup>. The Co 2p region (Fig. S2b) exhibits peaks at 781.2 and 796.8 eV with satellites at 786.7 and 803.0 eV, indicating mixed  $\text{Co}^{2+}/\text{Co}^{3+}$  species<sup>47</sup>. The Al 2p peaks (Fig. S2c) at 69.3 and 74.6 eV correspond to  $\text{Al}(\text{OH})_3/\text{Al}_2\text{O}_3$ , while the O 1s spectra (Fig. S2d) show components at 531.0 and 532.8 eV from lattice oxygen, hydroxides, and adsorbed water<sup>48,49</sup>. The C 1s region (Fig. S2e) reveals contributions from  $\text{sp}^2\text{C}$  (284.5 eV) C-C/C-N (285.6 eV), C-O (286.6 eV), C=O (287.8 eV), O-C=O (289.1 eV), and a  $\pi-\pi^*$  satellite at 290.8 eV, consistent with carbonate-containing LDH structures<sup>46,50</sup>. The carbon contribution is consistent with the interlayer  $\text{CO}_3^{2-}$  anions expected in LDH structures and already observed in FTIR and Raman analyses. Collectively, these data confirm the incorporation of Ni, Co, and Al into the hydrotalcite lattice with well-defined mixed-valence states.

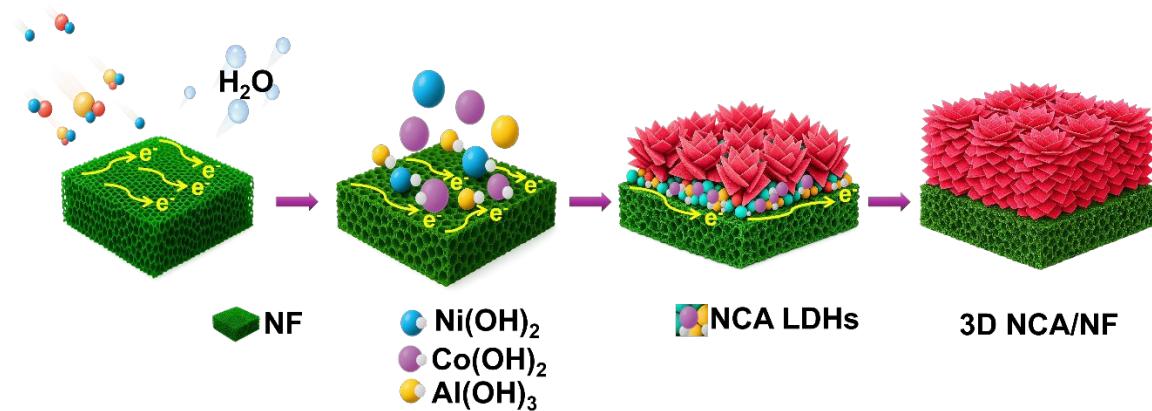
### 3.2. Morphological Characterization

The FE-SEM images (Fig. 2a-f) reveal that all LDH/NF electrodes adopt a 3D microflower-like morphology composed of self-assembled hexagonal nanosheets. These 3D-microflower architectures are uniformly anchored on the nickel foam (NF) substrate through one-step hydrothermal process, where urea ( $\text{CH}_4\text{N}_2\text{O}$ ) and ammonium fluoride ( $\text{NH}_4\text{F}$ ) acts as structure-

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directing agents. The growth proceeds (Scheme 1) via an integrated mechanism involving homogeneous precipitation, Ostwald ripening, and nanosheet self-assembly, consistent with the previous reports<sup>17,51</sup>. A detailed discussion of the growth mechanism is provided in the SI (Section S2). A hydrothermal duration of 15 h yields optimally developed NCA 3D microflowers uniformly covering NF, whereas shorter (5h) or longer reaction times (25h) led to incomplete formation or excessive aggregation of nanosheets (Fig. S3), respectively.

The EDX spectra and elemental mapping (Fig. S4) provide clear evidence of the successful synthesis of NiAl, CoAl and NiCoAl LDH phases, on the NF substrate. The recorded Ni weight percentages (77.01 % for NA/NF, 44.83 % for CA/NF and 54.08 % for NCA/NF) reflect combined contributions from Ni incorporated within the LDH lattices and from the underlying NF substrate. To quantitatively distinguish the intrinsic elemental composition of the synthesized LDHs independent of from substrate-derived contributions, powder EDX analyses (Fig. S5) were performed on the residual LDH precipitates collected from the hydrothermal autoclave after the in-situ growth process. Together, the elemental mapping (inset of Fig S3(a-c)), substrate supported EDX profiles and powder phase EDX analysis corroborate the successful formation of the intended NiAl, CoAl and NiCoAl LDH phases and establish that these materials grow uniformly and coherently on the Ni foam support.

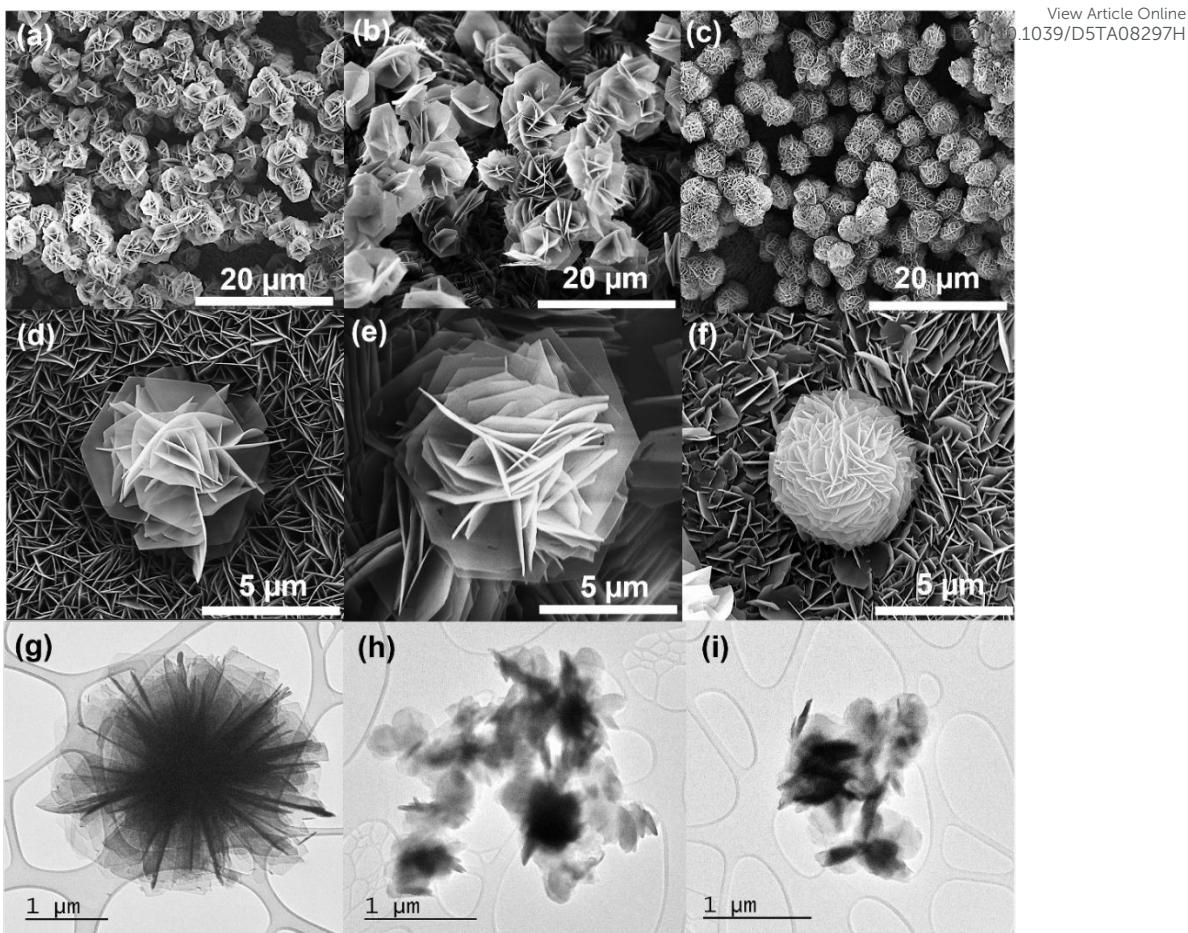


**Scheme. 1** Illustration of 3D NCA/NF formation.

The Histogram analysis (Fig. S6a-f) shows that the nanosheet edge length is shortest for NA/NF (0.95  $\mu$ m), significantly larger for CA/NF (4.4  $\mu$ m), and intermediate for NCA/NF (2.14  $\mu$ m). Thicknesses remain relatively uniform, averaging 27 nm for NA/NF and NCA/NF, and 44 nm for CA/NF. These results highlight strong compositional control over nanosheet evolution: Ni-Al LDH yields smaller and thinner nanosheets, Co-Al LDH forms comparatively large and thick nanosheets, while the ternary Ni-Co-Al LDH suppresses excessive lateral growth yet

maintains ultrathin thickness<sup>52</sup>. This balanced Ni:Co ratio promotes compact nucleation, restricts uncontrolled lateral expansion, and produces a denser nanosheet network compared to CA/NF. The architecture of NCA/NF is highly favourable for exposing electrochemically active sites and facilitating charge transport<sup>52,53</sup>.

The TEM images (Fig. 2g-i) further corroborate the FE-SEM results, confirming the hierarchical microflower structures of NCA/NF, CA/NF, and NA/NF. HRTEM (Fig. S7a-c in the SI) provides further structural insight. For NCA/NF, distinct lattice fringes with an interplanar spacing of 0.367 nm are observed, which can be indexed to the (006) plane of NiCoAl-LDH. The corresponding SAED pattern (Fig. S7d-f) displays sharp diffraction rings, confirming the high crystallinity of the ternary LDH<sup>49–51</sup>. Similarly, HRTEM images of NA/NF and CA/NF reveal lattice spacings of 0.382 nm and 0.228 nm, corresponding to the (006) plane of NiAl-LDH and the (015) plane of CoAl-LDH, respectively. Their SAED patterns show well-defined diffraction rings that confirm ordered crystalline domains, consistent with the layered double hydroxide structure. Specifically, the (006) and (110) planes are resolved for NiAl-LDH, the (006) and (015) planes are observed for CoAl-LDH<sup>24,54,55</sup>. These structural findings are consistent with XRD and Raman analyses, where the diffraction peaks corresponding to the (003), (006), and (110) planes and the Raman bands associated with M-O and O-M-O vibrations confirm the formation of well-crystallized LDH/NF phases. The lattice fringes observed in the HRTEM images exhibit d-spacing values consistent with those calculated from the corresponding XRD planes, confirming the phase purity and crystallographic integrity of the synthesized NCA/NF electrode. The Nitrogen adsorption-desorption measurements (Fig. S8) reveal that NCA/NF, CA/NF and NA/NF electrodes are mesoporous, exhibiting type IV isotherms<sup>56</sup>. The BET surface areas are 25.4, 21.3, and 19.2 m<sup>2</sup>g<sup>-1</sup> for NCA/NF, CA/NF, and NA/NF, respectively, with BJH pore size distribution showing pores mainly in the 16–20 nm range. The intrinsic macroporosity of the NF substrate, combined with the mesoporous NCA LDH network, provides a hierarchical pore architecture that facilitates electrolyte infiltration and ion transport, thereby enhancing overall electrochemical accessibility.



**Fig. 2.** FE-SEM images of (a, d) NCA/NF, (b, e) CA/NF, and (c, f) NA/NF; and TEM images of (g) NCA/NF, (h) CA/NF, and (i) NA/NF.

Therefore, the structural, chemical, and morphological features confirm the successful formation of NCA/NF electrodes with well-defined crystallinity, stabilized interlayer ( $\text{CO}_3^{2-}/\text{H}_2\text{O}$ ) species, mixed-valence ( $\text{Ni}^{2+}/\text{Ni}^{3+}$  and  $\text{Co}^{2+}/\text{Co}^{3+}$ ) states, and hierarchical 3D-microflower assemblies. These characteristics arise directly from the hydrothermal chemistry, where urea hydrolysis gradually supplies  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  while generating  $\text{NH}_3$ , which coordinates with  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Al}^{3+}$  to form stable complexes. The controlled release of metal cations and hydroxide ions promotes homogeneous nucleation, while  $\text{NH}_4\text{F}$  further regulates pH and directs anisotropic crystal growth. Under these conditions, nanosheets self-assemble through Ostwald ripening into uniform 3D microflower architectures anchored on NF. This “house-of-cards” stacking of microflower-like nanosheets generates interconnected mesopores, enhancing electrolyte accessibility, ion transport and overall electrochemical charge-storage and conversion efficiency<sup>21,56,57</sup>.

### 3.3. Electrochemical performance in a three-electrode system

Following the structural and compositional characterization, the electrochemical performance of the synthesized LDH electrodes (NA/NF, CA/NF, and NCA/NF) was investigated using CV, GCD, and EIS in 1 M KOH (Fig. 3a). The CV profile of NCA/NF (Fig. 3b) exhibits two distinct redox couples ( $\text{Ni}^{2+}/\text{Ni}^{3+}$  and  $\text{Co}^{2+}/\text{Co}^{3+}$ ) with markedly higher current density compared to NA/NF and CA/NF (Fig. S9a-e), evidencing the synergistic contribution of Ni, Co, and Al metals to enhanced redox-activity beyond binary LDHs. The observed pseudocapacitance arises from sequential charge-transfer processes, in which Ni and Co centres undergo the following valence-state transitions shown in equations (1-3),



At higher scan rates, the oxidation peaks of NCA/NF shift positively, indicative of restricted ion penetration into the inner sites of the microflower architecture. In contrast, lower scan rates enable more effective ion access, thereby enhancing redox utilization. This trend is consistent with the current response at 20 mV s<sup>-1</sup>, where bare NF delivers an anodic peak current density of only 3 mA g<sup>-1</sup>, whereas NA/NF, CA/NF and NCA/NF reach 59.1, 120.1 and 175.2 mA g<sup>-1</sup>, respectively (Fig. S10a-b). Notably, NCA/NF exhibits the highest anodic current density among the electrodes studied, reflecting enhanced redox activity arising from the synergistic interplay of Ni, Co, and Al within the layered structure. The contribution from the nickel foam substrate is negligible, as indicated by the minimal current response of bare NF under identical conditions. This confirms that the electrochemical behaviour is dominated by the active LDH material.

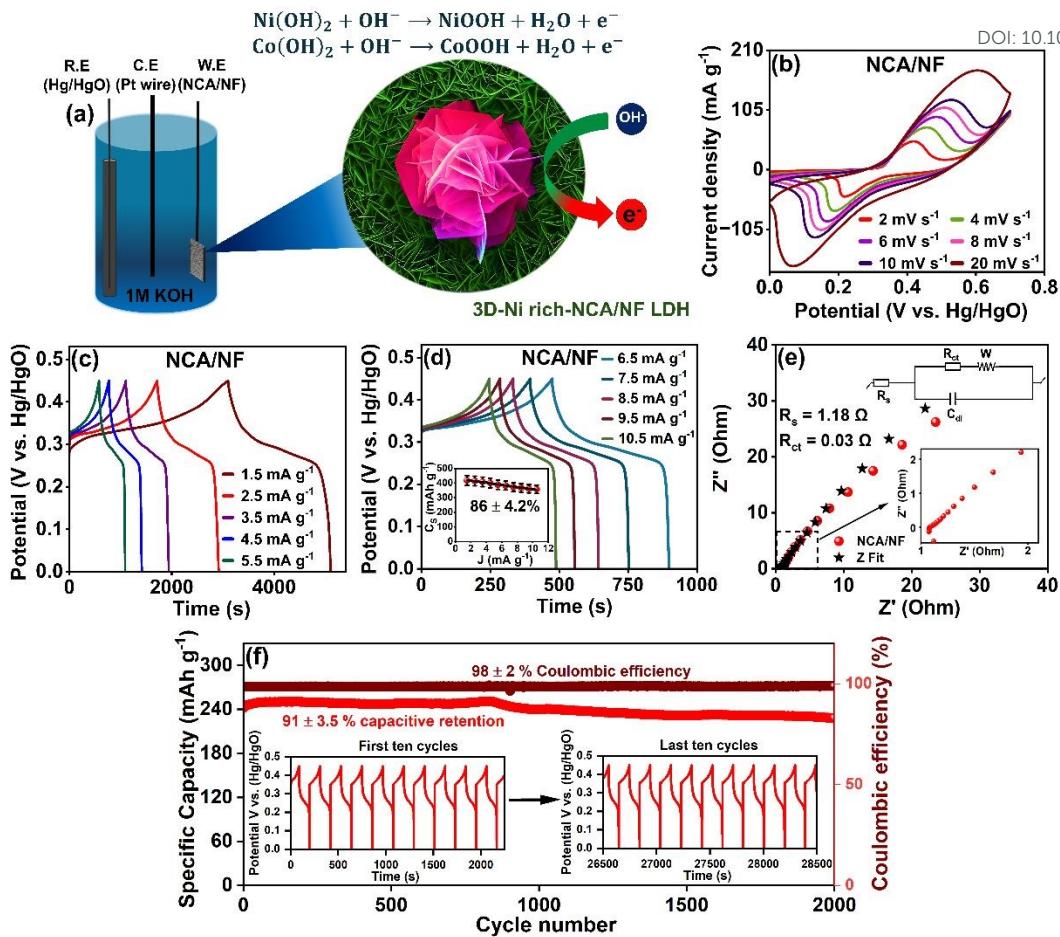
Kinetic analysis (Fig. S11 and S12) confirms that the NCA/NF electrode exhibits a dominant pseudocapacitive contribution, increasing from 43% at 2 mV s<sup>-1</sup> to 75% at 20 mV s<sup>-1</sup>. In comparison, NA/NF exhibits more diffusion-controlled behaviour, while NCA/NF and CA/NF show pseudocapacitive behaviour. The higher pseudocapacitive fraction of NCA/NF explains its superior redox activity, rate capability, and cycling stability. Full details of the b-value determination and capacitive/diffusion contribution analysis are provided in the SI (Fig. S11 and S12; Equations S13-S14). The GCD analysis (Fig. 3c-d) highlights the outstanding performance of NCA/NF electrode, delivering a high specific capacity of 3346 F g<sup>-1</sup> (418 mAh g<sup>-1</sup>) at 1.5 A g<sup>-1</sup> and retaining 2863 F g<sup>-1</sup> (358 mAh g<sup>-1</sup>) at 10.5 A g<sup>-1</sup> (86% retention; Fig. 3d,



inset). The comparative GCD profiles of NCA/NF, NA/NF, and CA/NF electrodes are provided in the SI (Fig. S9f-i). At  $1.5 \text{ mA g}^{-1}$ , NA/NF and CA/NF delivered  $2262 \text{ F g}^{-1}$  and  $1757 \text{ F g}^{-1}$  ( $249$  and  $281 \text{ mAh g}^{-1}$ ), respectively, with significantly lower rate capability retentions of  $58\%$  and  $46\%$  (Fig. S9j). To provide a practical assessment of electrode-level performance, the areal capacitances were calculated using the geometric area ( $1 \times 1 \text{ cm}^2$ ) and an active mass loading of  $1.5 \text{ mg cm}^{-2}$ . Bare Ni foam ( $1 \times 1 \text{ cm}^2$ ) shows negligible intrinsic contribution, delivering only  $24$  to  $16 \text{ mF cm}^{-2}$  over  $1.5$  -  $5.5 \text{ mA cm}^{-2}$  (Fig. S10c-d). In contrast, the NA/NF, CA/NF and NCA/NF electrodes achieve substantially higher areal capacitances of approximately  $3393 \text{ mF cm}^{-2}$ ,  $2636 \text{ mF cm}^{-2}$  and  $5019 \text{ mF cm}^{-2}$ , respectively, at  $1.5 \text{ mA cm}^{-2}$ , which correspond directly to their gravimetric capacities. These values exceed the bare NF baseline by nearly two orders of magnitude, confirming that the enhanced charge storage originates predominantly from the LDH architectures rather than the substrate.

To clarify the correlation between the hierarchical NCA/NF architecture and its charge-transport characteristics, the EIS response was fitted using a Randles-type equivalent circuit (Fig. 3e). The simulated impedance profile (Z Fit) shows almost a complete overlap with the experimental Nyquist plot, indicating excellent fitting fidelity and minimal residuals. This agreement confirms that the selected circuit reliably captures the electrode's impedance behaviour. The NCA/NF electrode delivers an exceptionally low charge-transfer resistance ( $R_{ct} = 0.025 \Omega$ ), lower than NA/NF ( $0.031 \Omega$ ) and CA/NF ( $0.036 \Omega$ ) (Fig. S9k), indicating fast charge-transfer kinetics at the electrode/electrolyte interface. The combined effects of its ultrathin ( $27 \text{ nm}$ ) nanosheet layers and interconnected 3D microflower affords continuous electron pathways while promoting rapid  $\text{OH}^-$  transport through mesoporous channels ( $16$ - $20 \text{ nm}$ ). This response reflects sufficiently rapid ion transport through the mesoporous hierarchical architecture, resulting in a negligible Warburg contribution. The electrochemical performance of NCA/NF in a three-electrode configuration with KOH electrolyte surpasses most of the previously reported NiCoAl-based systems (Table S1), highlighting its exceptional intrinsic electrochemical activity.

Long-term cycling performance (Fig. 3f) further demonstrates that the NCA/NF electrode retains  $91\%$  of its initial capacity after  $2000$  cycles. Importantly, the NCA/NF electrode also maintains a high Coulombic efficiency of  $98\%$  throughout cycling, indicating excellent charge/discharge reversibility. In contrast, the NA/NF and CA/NF electrodes (Fig. S9l) retain only  $37\%$  and  $56\%$  of their initial capacities, respectively.



**Fig. 3** (a) Representation of three electrode setup (b) CV curves (2 to 20 mV s<sup>-1</sup>), (c) GCD (1.5 to 5.5 mA g<sup>-1</sup>), (d) GCD (6.5 to 10.5 mA g<sup>-1</sup>) (inset graph represents rate capability retention; error bars have been added based on triplicate measurements), (e) Nyquist plot with Z Fit (inset graph represents the Nyquist plot in the high frequency region), with only minute variability (0.001 Ω) across repeated measurements and (f) Stability curve (2000 cycles) of NCA/NF LDH electrode; where the continuous nature of the curve does not permit conventional error bars instead, standard deviation values are provided to quantify variability in cyclic stability and Coulombic efficiency.

Post-cycling structural and morphological studies were conducted. FE-SEM (Fig. S13a-c) shows that NCA/NF retains its characteristic 3D microflower architecture after 2000 charge/discharge cycles, while NA/NF and CA/NF suffer pronounced delamination from the NF substrate. NCA/NF maintains strong adhesion, ensuring continuous ion/electron transfer pathways and structural stability. Further, EDX mapping (Fig. S13d-f) reveals increased oxygen content along with trace amounts of potassium across all electrodes, suggesting surface oxidation and the presence of residual electrolyte species. In addition, post-electrochemical characterization provides further evidence of the preserved structural integrity and stability of the electrodes. The CV curves of NA/NF and CA/NF (Fig. S14a-b) exhibit a decline in redox



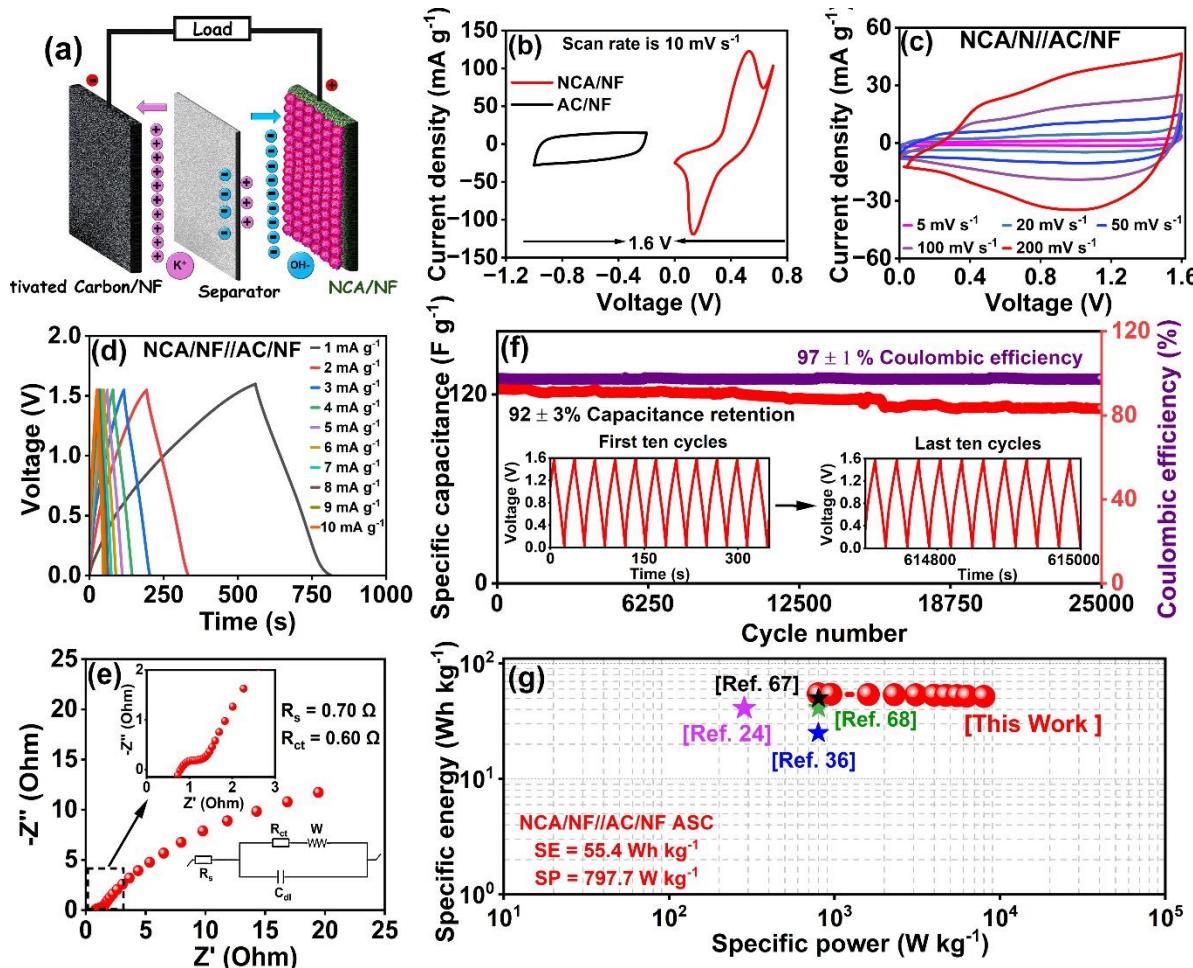
current density, reflecting partial degradation and loss of active sites, whereas NCA/NF (Fig. S14c) largely preserves its redox profile with only minor attenuation. The EIS analysis (Fig. S14d) reveals a slight increase in charge-transfer resistance for NCA/NF (Table S2), attributable to benign surface passivation or nanosheet densification, changes that do not compromise its electrochemical activity.

The exceptional electrochemical performance of the NCA/NF electrode stems from its Co-lean, Ni-rich composition and binder-free architecture. Abundant  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox sites deliver high Faradaic capacity, while limited Co incorporation enhances charge-transfer kinetics and structural stability through  $\text{Co}^{2+}/\text{Co}^{3+}$  couples<sup>58</sup>. Though electrochemically inactive,  $\text{Al}^{3+}$  stabilizes the layered framework, promotes higher-valence  $\text{Ni}^{3+}/\text{Co}^{3+}$  formation, and improves ionic conductivity<sup>59</sup>. In hydrotalcite-like Ni-Co-Al LDHs,  $\text{Al}^{3+}$  functions as the trivalent  $\text{M}^{3+}$  species that generates the positive layer charge and stabilises the brucite-like host layers, rather than contributing a separate redox couple<sup>60,61</sup>. Prior studies on NiCoAl systems have shown that introducing  $\text{Al}^{3+}$  enhances structural ordering and promotes the formation of robust nanosheet architectures with improved mechanical integrity<sup>62</sup>. These studies collectively demonstrate that  $\text{Al}^{3+}$  acts as a structural and electronic stabiliser by governing the layer charge, tuning the transition-metal (Ni/Co) coordination framework, and preserving the hierarchical LDH architecture, thereby enabling the high redox utilisation and cycling stability observed in the NCA/NF electrodes. The hierarchical 3D microflower morphology, directly grown on conductive NF without additives, ensures intimate contact, low resistance, and efficient ion/electron transport. Together, these features endow NCA/NF with high capacity, rapid kinetics, and exceptional cycling durability, making it a robust, sustainable electrode for advanced asymmetric supercapacitors.

### 3.4. Electrochemical performance in a two-electrode system

Owing to its superior three-electrode performance, NCA/NF was selected as the positive electrode in an ASC, paired with AC/NF as the negative electrode (Fig. 4a). The device was assembled in a PAT-core cell using 1 M KOH electrolyte and a GFM separator. CV analysis established an optimal operating window of 1.6 V, beyond which polarization from oxygen evolution was observed (Fig. S15a). Within this range, the CV profile (Fig. 4b) display the hybrid behaviour characteristic of an ASC, arising from the double-layer capacitance of AC and the pseudocapacitance of NCA. The NCA/NF//AC/NF full cell (Fig. 4c) was recorded at

various scan rates from 5 to 200 mV s<sup>-1</sup> within a potential window of 0-1.6 V. The CV curves exhibit quasi-rectangular shapes with slight redox humps, indicative of a combined capacitive and Faradaic charge-storage mechanism.



**Fig. 4** (a) Illustration of asymmetric supercapacitor (b) The Voltage window of AC/NF and NCA/NF at 10 mV s<sup>-1</sup> (c) CV curves at various scan rates (5-200 mV s<sup>-1</sup>), (d) GCD curves at various current densities (1 to 10 mA g<sup>-1</sup>), (e) Nyquist plot, (f) Cycling Stability; Standard deviations are shown to indicate electrode to electrode variability in cyclic stability and Coulombic efficiency, (g) Ragone plot of NCA/NF//AC/NF ASC device.

Notably, the profile remains well preserved even at high scan rates, accompanied by a proportional rise in current response, confirming excellent rate capability. Moreover, GCD profile (Fig. 4d) confirm high charge storage, delivering 156.25 F g<sup>-1</sup> at 1 mA g<sup>-1</sup> and 143.75 F g<sup>-1</sup> at 10 mA g<sup>-1</sup>, corresponding to 92% rate capability retention (Fig. S15b). The EIS analysis (Fig. 4e) reveals low series and charge-transfer resistances ( $R_s = 0.70 \Omega$ ,  $R_{ct} = 0.60 \Omega$ ), ensuring efficient ion /electron transport. All ASC performance metrics were determined using the combined active mass of both electrodes (4.0 mg), with all calculations conducted using an IR-



drop-corrected operating window of 1.6 V. The raw GCD discharge curve with the annotated IR drop is provided in Fig. S16a-b, and full calculation details including the worked capacitance/energy example and mass-balancing derivation are presented in Section S3.1 (SI).

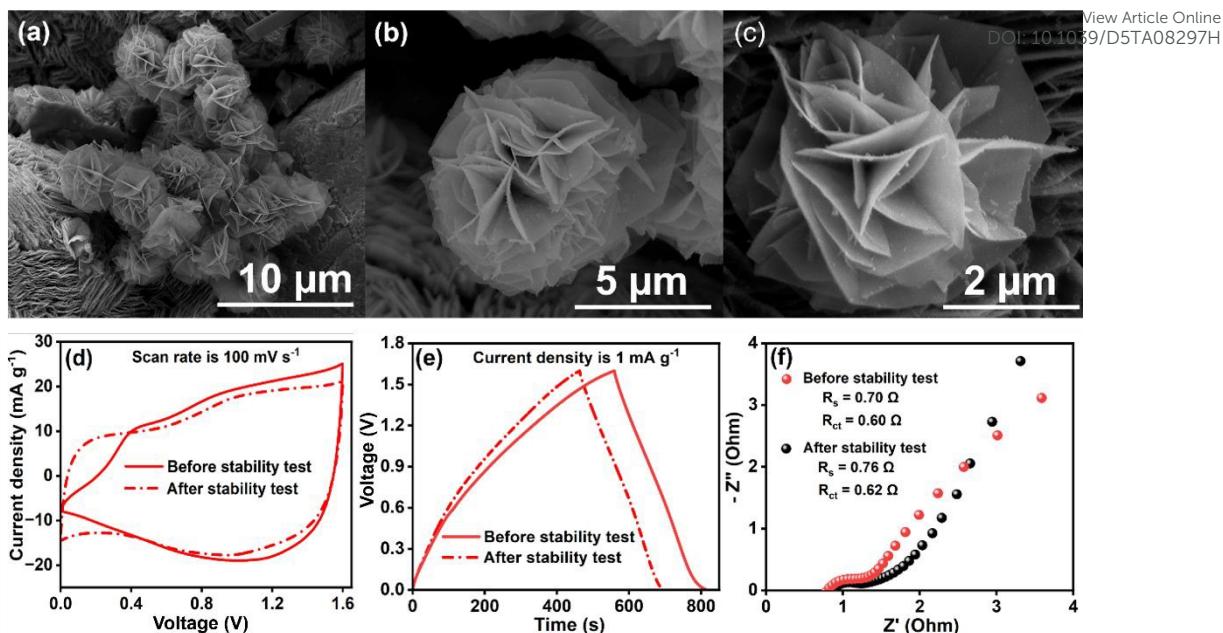
Long-term durability is equally notable, with the ASC retaining 92% of its initial capacitance after 25,000 cycles at 10 mA g<sup>-1</sup> (Fig. 4f), while sustaining a Coulombic efficiency of 97%, indicating highly reversible charge-discharge behaviour throughout prolonged cycling. The Ragone plot (Fig. 4g) highlights a specific energy 55.4 Wh kg<sup>-1</sup> at a specific power of 797.7 W kg<sup>-1</sup> at 1 mA g<sup>-1</sup>. The NCA/NF positive electrode is composed of nickel, cobalt, and aluminium in a molar ratio of 4:2:1, with a loading of 1.5 mg cm<sup>-2</sup>, corresponding to 0.88 mg of Ni, 0.47 mg of Co, and 0.17 mg of Al per device. Cobalt contributes only a minor fraction (6.4 Wh kg<sup>-1</sup> and 92.5 W kg<sup>-1</sup>) of the energy and power, while nickel provides most of the faradaic charge-storage capability, and aluminium acts primarily as a structural stabilizer. These contributions are calculated based on the mass fractions of Ni and Co in the positive electrode, reflecting their proportional contributions to the faradaic energy and power. The negative electrode, AC/NF, contributes capacitive charge storage that complements the faradaic energy of the Ni-rich positive electrode. Compared with cobalt-richer analogues reported in the literature<sup>25,63-66</sup> that deliver similar or lower specific energy and power, the Ni-rich, Co-lean NCA/NF electrode achieves higher energy and power output, providing a quantitatively supported sustainability advantage. This demonstrates that the NCA/NF electrode design employed here enables cobalt to function primarily as an electronic and kinetic facilitator rather than the dominant charge-storage species, achieving high performance with minimal cobalt usage. Also, the device still delivered 51.1 Wh kg<sup>-1</sup> at 10 mA g<sup>-1</sup>, even at a high specific power of 7998.2 W kg<sup>-1</sup>, highlighting excellent rate capability and strong energy retention under high-power operation. This energy-power-lifetime balance outperforms most reported NiCoAl LDH based ASCs (Table 1).

**Table 1.** Electrochemical parameters of NCA/NF//AC ASC compared with recent reports

Anode//Cathode	Electrolyte (KOH)	Capacitance (F g <sup>-1</sup> )	Specific energy (Wh kg <sup>-1</sup> )	Specific power (KW kg <sup>-1</sup> )	Capacity retention (Stability Cycle)	Ref
Ni <sub>1</sub> Co <sub>2</sub> Al <sub>1</sub> -LDHs//AC	6 M	117.83 at 1 A g <sup>-1</sup>	41.8	0.8	92.5% (2800)	<sup>67</sup>
NiCo <sub>2</sub> Al <sub>0.5</sub> //AC	3 M	109.56 at 1 A g <sup>-1</sup>	39	0.8	91.7% (6000)	<sup>36</sup>
NiCoAl-LDH/NF//PAC	3 M	116.56 at 1 A g <sup>-1</sup> ,	41.44	0.2842	81.6% (6000)	<sup>24</sup>
NCAL 13//AC	3 M	150 at 1 A g <sup>-1</sup>	50	2.30	86% (10000)	<sup>68</sup>
NiCoAl-OH//AC	6 M	120.4 at 1 A g <sup>-1</sup>	68.5	0.256	94.1% (10000)	<sup>61</sup>
C-NCA//AC	6 M	212.5 at 1 A g <sup>-1</sup>	75.55	0.8	89.87 (2000)	<sup>23</sup>
<b>NCA/NF//AC/NF</b>	<b>1 M</b>	<b>156.25 at 1 mA g<sup>-1</sup></b>	<b>55.4</b>	<b>797.7</b>	<b>92% (25000)</b>	<b>This work</b>

Post-cycling characterizations of the cycled NCA/NF electrode validates this electrochemical robustness. FE-SEM images (Fig. 5a-c) reveal that the 3D microflower morphology remains intact even after 25,000 cycles, demonstrating strong structural integrity. Correspondingly, the CV and GCD profiles obtained after the stability test (Fig. 5d-f) show negligible deviation further confirming the preservation of structure and electrochemical performance. The EDX spectra (Fig. S17) of the cycled electrode show potassium residues, attributable to alkaline electrolyte by-products such as K<sub>2</sub>CO<sub>3</sub> formed when KOH absorb atmospheric CO<sub>2</sub>. These surface-bound species do not disrupt the electrode architecture<sup>69</sup>. A slight oxygen enrichment is consistent with the M(OH)<sub>2</sub> to MOOH (M = Ni, Co), a well-known transformation that generates the active oxyhydroxide phase mediating pseudocapacitive redox reactions, rather than indicating degradation<sup>70-72</sup>. Together, these findings confirm that NCA/NF maintains its hierarchical framework, and electrochemical functionality over prolonged cycling, underpinning its high energy density and stability<sup>73</sup>.



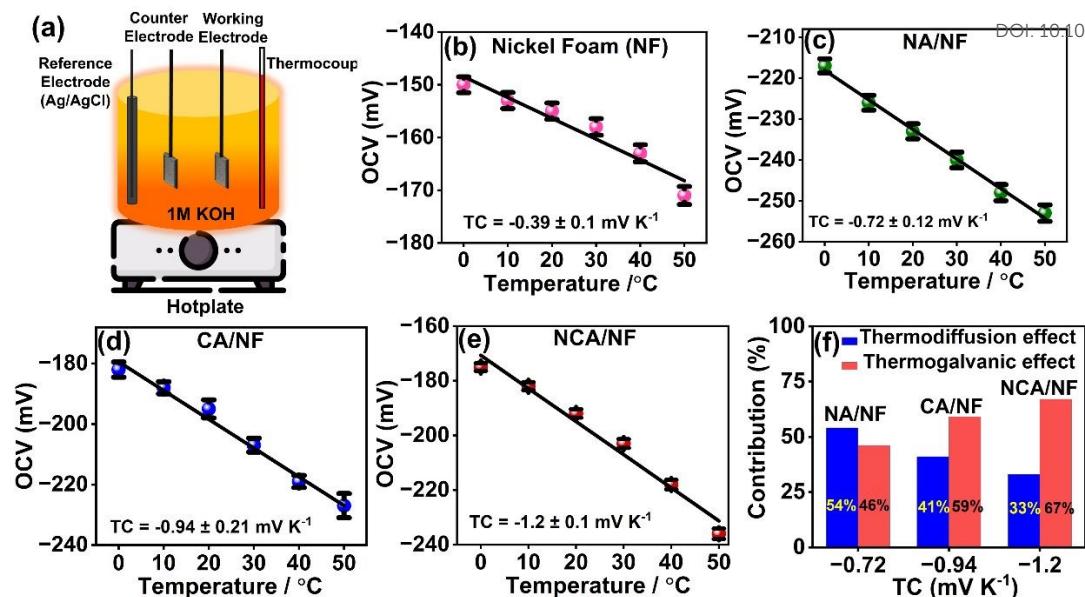


**Fig. 5.** Post-cycling characterization of the NCA/NF electrode after 25,000 cycles: (a-c) FE-SEM images, (d) CV profiles, (e) GCD curves, (f) EIS spectra before and after cycling.

The outstanding performance of the NCA/NF//AC/NF ASC can be attributed to four synergistic factors: (i) binder-free growth on Ni foam, ensuring intimate electrical contact and robust adhesion; (ii) the 3D microflower architecture, which offers a high surface area and efficient ion diffusion pathways; (iii) the Ni-rich composition, which supplies abundant  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox sites, while moderate Co content enhances conductivity and  $\text{Al}^{3+}$  stabilizes the layered framework against dissolution<sup>24,45,60</sup> and (iv) the asymmetric pairing with AC, which balances charge kinetics across the extended 1.6 V operating window. Collectively, these features provide high energy density, rapid charge-discharge capability, and exceptional long-term cycling stability, establishing Co-lean NCA/NF as a highly durable and efficient electrode material for next-generation hybrid energy storage and conversion devices.

### 3.5. Thermoelectrochemical cell

In line with the outstanding performance of NCA/NF as an electrode for ASC, its exceptional properties were explored in TEC applications. As the overall TEC response results from the combined influence of ionic thermodiffusion and redox-driven thermogalvanic effects, isothermal measurements (Fig. 6a) were employed to decouple these contributions and identify the dominant mechanism governing the electrode behaviour. During these tests, the electrode potential was monitored under uniform temperature increase (20 to 70 °C).



**Fig. 6** (a) Schematic representation of isothermal characterization, Open-circuit voltage as a function of electrolyte temperature for (b) Bare NF, (c) NA/NF (d) CA/NF, and (e) NCA/NF electrode systems; (b-e) Data points represent mean values from replicate measurements ( $n = 3$ ), with error bars showing the standard deviation (SD). Linear fits are provided to extract the temperature coefficient and (f) Fractional contributions of various thermal processes.

The stepwise isothermal control measurements used to obtain the temperature coefficients (TCs) in Fig. 6(b-e), which shows a smooth and reproducible change in OCV with increasing uniform temperature for all electrodes (Fig. S18(a-d)). The OCV follows a clear step-by-step trend with unexpected shifts which is consistent with previous reports<sup>74-76</sup>. This confirms that the temperature-dependent behaviour reflects the intrinsic properties of each electrode and is not affected by bulk heating effects. The resulting isothermal baseline provides a reliable foundation for the temperature-coefficient analysis presented in Fig. 6b-e.

This approach allows clear distinction between simple electrolyte ion migration and entropy-rich redox reactions that contribute to the overall thermoelectrochemical response. Following the method established from previous reports<sup>75,77</sup>, the TCs were determined for each electrode. The bare NF exhibited a TC of  $-0.39 \text{ mV K}^{-1}$  (Fig. 6b), characteristic of pure ionic thermodiffusion. In contrast, the LDH-based electrodes showed higher values of  $-0.72 \text{ mV K}^{-1}$  (NA/NF),  $-0.94 \text{ mV K}^{-1}$  (CA/NF), and  $-1.2 \text{ mV K}^{-1}$  (NCA/NF) (Fig. 6c-e), reflecting enhanced redox-driven thermogalvanic contributions. Subtracting the NF baseline yields net redox-driven contributions of  $-0.33$ ,  $-0.55$ , and  $-0.81 \text{ mV K}^{-1}$  for NA/NF, CA/NF, and NCA/NF, respectively, indicating stronger redox entropy contributions. These contributions were further

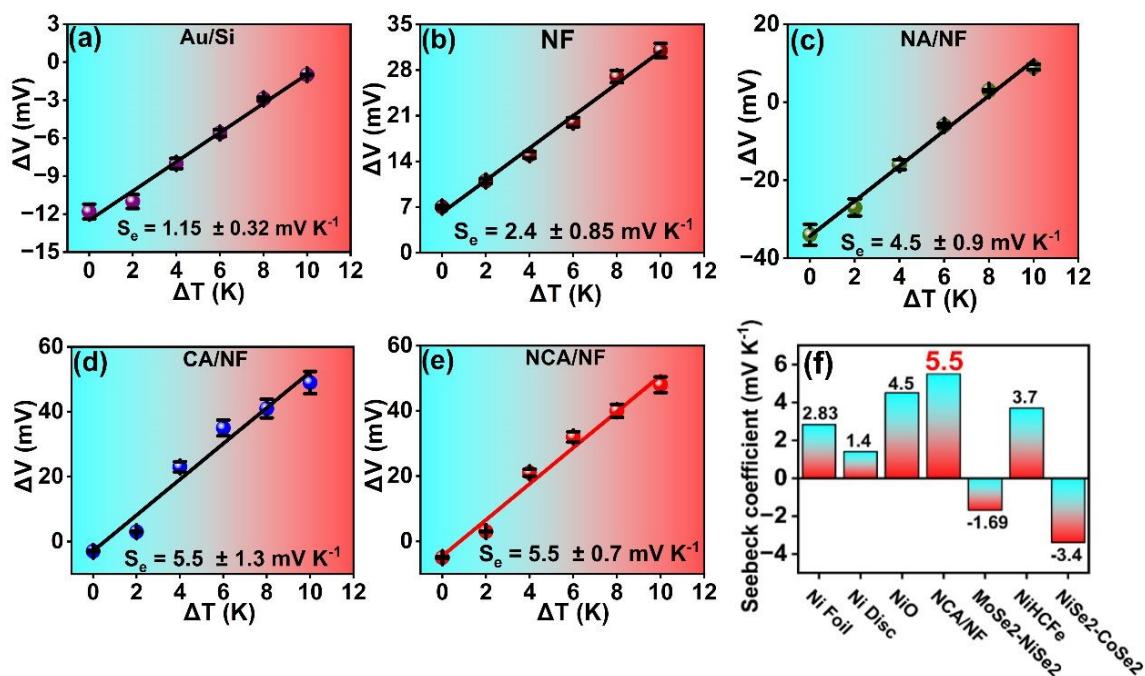
quantified using the relationships described<sup>75,76</sup> in SI (Section 3.2). Quantitative partitioning (Fig. 6f) revealed thermodiffusion and thermogalvanic fractions of 54/46 % for NA/NF, 41/59 % for CA/NF, and 33/67 % for NCA/NF. While this analysis effectively isolates the entropy-related redox component, complementary non-isothermal TEC measurements are required to evaluate the practical heat-to-electricity conversion efficiency.

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Non-isothermal performance was evaluated using thermoelectric cell configuration (Fig. S19), where a temperature gradient ( $\Delta T$ ) across the electrodes were employed to determine the ionic Seebeck coefficient ( $S_e$ ) and thermal charge storage ( $J$ ). Thermodynamically,  $S_e$  is governed by the entropy change ( $\Delta S$ ) of the redox reactions according to the following equation,

$$S_e = \frac{\Delta S}{nF} \quad (4)$$

where  $n$  is the number of electrons transferred per reaction and  $F$  is the Faraday constant.



**Fig. 7** Non-isothermal Seebeck voltage as a function of temperature gradient for (a) Au/Si wafer, (b) bare NF, (c) NA/NF, (d) CA/NF, and (e) NCA/NF electrodes; Error bars represent mean  $\pm$  SD from replicate measurements ( $n = 3$ ). Linear fits are shown with 95 % confidence intervals. (f) Comparison of Seebeck coefficients for various Ni-based electrodes, highlighting the superior performance of NCA/NF.

Here, the redox asymmetry induced by  $\Delta T$  promotes oxidation at the hot electrode ( $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$ ;  $\text{Co}^{2+} \rightarrow \text{Co}^{3+}/\text{Co}^{4+}$ ) and reduction at the cold electrode, while  $\text{OH}^-$  ions shuttle across the electrolyte (Fig. S20). Calibration electrodes (Au/Si and bare NF) yielded  $S_e$  values of 1.5 and 2.4 mV K $^{-1}$  (Fig. 7a-b), consistent with literature reports<sup>78,79</sup>. All three LDH/NF electrodes exhibited distinct thermoelectrochemical behaviour, with the  $S_e$  values increasing from 4.5 mV K $^{-1}$  (NA/NF) to 5.5 mV K $^{-1}$  (CA/NF and NCA/NF), accompanied by corresponding thermal charge storage values of 1.35 J (NA/NF) and 1.65 J (CA/NF and NCA/NF) (Fig. 7c-e). Isothermal control measurements confirmed that the  $S_e$  arises primarily from thermogalvanic redox reactions, as thermodiffusion contributes only tens of  $\mu\text{V K}^{-1}$ , negligible compared to the millivolt-level signal. Also, the polarity of the Peltier heater/cooler connections was reversed to interchange hot and cold sides. The resulting Seebeck coefficients of LDH/NF electrodes (Fig. S21 a-c) remain consistent with the measurements shown in Fig. 7c-e. This confirms that the observed thermal voltage originates from the ionic Seebeck effect of the LDH/NF electrodes, rather than from measurement artefacts or parasitic potentials. When benchmarked against Ni based thermogalvanic systems (Fig. 7f, Table 2)<sup>21,79-82</sup>, the  $S_e$  of NCA/NF (5.5 mV K $^{-1}$ ) surpasses most state-of-the-art electrode materials, establishing it as a highly efficient bi-functional platform capable of simultaneous low-grade heat harvesting and electrochemical energy storage.

**Table 2.** Comparing the Seebeck coefficient ( $S_e$ ) of Ni based electrodes with the present study.

S.no	Electrodes	Cell type	Electrolyte	$S_e$ (mV K $^{-1}$ )	Ref.
1	Nickel Foil	Beakers + salt bridge	1 M $\text{NiSO}_4$	2.83	<sup>79</sup>
2	Nickel Disc	Cylindrical TEC	0.4 M $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$	1.4	<sup>80</sup>
3	NiO Microsphere	Beakers + salt bridge	6 M KOH	4.5	<sup>81</sup>
4	MoSe <sub>2</sub> -NiSe/NF	Beakers + salt bridge	0.4 M $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$	-1.69	<sup>82</sup>
5	NiSe <sub>2</sub> -CoSe <sub>2</sub> nanowires	ASTM D5470-06	1 M NaOH	-3.4	<sup>21</sup>
6	<b>NCA/NF</b>	<b>TEC</b>	<b>1 M KOH</b>	<b>5.5</b>	<b>This Work</b>

The comparatively high Seebeck coefficient obtained for the NCA/NF electrode, relative to previously reported Ni-based thermogalvanic systems (Fig. 7f, Table 2), can be attributed to the synergistic effects of its tailored composition and nanoscale architecture. The Ni-rich, Co-lean mixed-valence environment increases the density of reversible  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox centres<sup>21,82</sup> while maintaining a smaller population of  $\text{Co}^{2+}/\text{Co}^{3+}$  sites. This composition enhances electronic coupling within the Ni-O-Co framework and facilitates more thermally responsive redox transitions at the hot electrode, yielding a larger intrinsic entropy change and, consequently, a higher ionic Seebeck coefficient. Incorporation of  $\text{Al}^{3+}$  into the layered lattice further stabilises the hydroxide sheets and increases the local polarisation of M-OH moieties<sup>52</sup>. This modification strengthens interactions with migrating  $\text{OH}^-$  species and perturbs the coordination and electronic structure of the LDH layers, thereby increasing the temperature dependence of  $\text{OH}^-$  adsorption/desorption and associated electron-transfer kinetics<sup>81</sup>. These effects collectively magnify the redox-potential difference established between the hot and cold electrodes.

The ultrathin LDH microflower morphology supported on the 3D nickel-foam scaffold provides an exceptionally high density of accessible redox sites and markedly reduced ion-diffusion distances. This architecture ensures that a larger proportion of thermogalvanic centres is engaged under an applied temperature gradient, leading to an amplified voltage response. Overall, these compositional and structural attributes generate a stronger temperature-dependent redox driving force than is typically observed in conventional Ni-based electrodes, consistent with the superior  $S_e$  values measured for NCA/NF. The robustness of this enhancement is confirmed by the control experiments: (i) isothermal tests showing stepwise OCV evolution with  $\Delta T$ , and (ii) polarity-reversal measurements yielding identical  $S_e$  values. These results affirm that the elevated  $S_e$  originates from the intrinsic thermogalvanic behaviour of NCA/NF rather than extrinsic or configuration-dependent artefacts. Collectively, the findings position NCA/NF as a highly efficient thermogalvanic material capable of surpassing state-of-the-art Ni-based systems for low-grade heat harvesting.

#### 4. Conclusions

The objective of this work is to design a bi-functional electrode capable of achieving ultrahigh electrochemical and thermoelectrochemical performance without external dopants, binders, or conductive additives. To achieve this, a Ni-Co-Al layered double hydroxide (NCA) was

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directly grown on nickel foam (NF) via a facile hydrothermal strategy, where precise control of the Ni:Co:Al ratio (4:2:1) produced a Ni-rich, Co-lean composition that maximized electroactive Ni site density while minimizing cobalt usage, thereby enhancing redox activity, sustainability, and cost efficiency. Controlled urea hydrolysis and transient F<sup>-</sup> coordination directed the assembly of ultrathin (27 nm) nanosheets into 3D hierarchical microflowers firmly anchored to the NF substrate, ensuring large electroactive surface area, efficient charge transport, and excellent structural stability. The resulting NCA/NF positive electrode exhibited outstanding bi-functionality, delivering a specific energy of 55.4 Wh kg<sup>-1</sup> in an asymmetric supercapacitor and a Seebeck coefficient of 5.5 mV K<sup>-1</sup> in a TEC, where the performance metrics rarely achieved in fully additive-free systems. The NCA/NF electrode also surpassed its binary analogues (NA/NF and CA/NF), confirming the synergistic advantage of ternary Ni-Co-Al chemistry in enhancing redox activity, conductivity, and long-term stability. The exceptional bifunctionality of the NCA/NF electrode arises from the synergistic interplay of structural, chemical, and compositional chemistry, validating the central hypothesis of this work. Each constituent metal contributes a distinct yet complementary role, i) Ni acts as the primary redox-active centre enabling reversible Ni<sup>2+</sup>/Ni<sup>3+</sup> transitions, ii) Co-lean composition modulates the local electronic environment, facilitates oxygen-vacancy formation, and accelerates charge transfer through Ni-O-Co bridges and iii) Al<sup>3+</sup> strengthens the layered lattice, maintaining structural integrity during prolonged cycling. Thereby, this study demonstrates that the Co-lean architecture, combined with the synergistic Ni-Co-Al chemistry and a dopant- and additive-free design, enables efficient oxygen-mediated redox processes and Ni-O-Co coordination, delivering ultrahigh electrochemical and thermoelectrochemical efficiencies. This pioneering, facile synthesis and electrode design approach, rooted in Ni-Co-Al chemistry, provides a sustainable and scalable framework for developing next-generation cobalt-lean electrodes for electrochemical energy storage and conversion devices.

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# Additive Free Co-Lean Ternary NiCoAl/Ni Foam Electrode for High-Efficiency Energy Storage and Low-Grade Heat Harvesting

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## Data Availability Statement

The datasets generated and analysis during this study will be available in the TRANSLATE Zenodo community (<https://zenodo.org/communities/translateh2020/>) upon publication of this article. All data supporting the findings will be assigned a DOI and made publicly accessible through this repository.

