Synthesis, Characterizations, and Electrochemical Performances of Highly Porous, Anhydrous Co\textsubscript{0.5}Ni\textsubscript{0.5}C\textsubscript{2}O\textsubscript{4} for Pseudocapacitive Energy Storage Applications

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**ABSTRACT:** Electrochemical energy storage relies essentially on the development of innovative electrode materials with enhanced kinetics of ion transport. Pseudocapacitors are excellent candidates to bridge the performance gap between supercapacitors and batteries. Highly porous, anhydrous Ni\textsubscript{0.5}Co\textsubscript{0.5}C\textsubscript{2}O\textsubscript{4} is envisaged here as a potential electrode for pseudocapacitor applications, mainly because of its open pore framework structure, which poses inherent structural stability due to the presence of planar oxalate anions (C\textsubscript{2}O\textsubscript{4}\textsuperscript{2−}), and active participation of Ni\textsuperscript{2+/3+} and Co\textsuperscript{2+/3+} results in high intercalative charge storage capacity in the aqueous KOH electrolyte. The Ni\textsubscript{0.5}Co\textsubscript{0.5}C\textsubscript{2}O\textsubscript{4} electrode shows specific capacitance equivalent to 2396 F/g at 1 A/g in the potential window of 0.6 V in the aqueous 2 M KOH electrolyte by galvanostatic charge/discharge experiments. Predominant pseudocapacitive mechanism seems to operate behind high charge storage due to active participation of Ni\textsuperscript{2+/3+} and Co\textsuperscript{2+/3+} redox couple as intercalative (inner) and surface (outer) charges stored by porous anhydrous Co\textsubscript{0.5}Ni\textsubscript{0.5}C\textsubscript{2}O\textsubscript{4} were close to high 38 and 62% respectively. Further, in full cell asymmetric supercapacitors (ASCs) in which porous anhydrous Co\textsubscript{0.5}Ni\textsubscript{0.5}C\textsubscript{2}O\textsubscript{4} was used as the positive electrode and activated carbon (AC) was utilized as the negative electrode, in the operating potential window 1.6 V, the highest specific energy of 283 W h/kg and specific power of ∼817 W/kg were achieved at 1 A/g current rates. Even at a very high power density of 7981 W/kg, the hybrid supercapacitor still attains an energy density of ∼75 W h/kg with high cyclic stability at a 10 A/g current rate. The detailed electrochemical studies confirm higher cyclic stability and a superior electrochemical energy storage property of porous anhydrous Co\textsubscript{0.5}Ni\textsubscript{0.5}C\textsubscript{2}O\textsubscript{4} making it a potential pseudocapacitive electrode for large energy storage applications.

**INTRODUCTION**

Uninterrupted fuel and power supply is a driving force for the innovations and growth of mankind to sustain modern civilization, and continuous depletion of natural sources of fossil fuels and associated environmental concerns has boosted the demand for sustainable, clean, and green energy generation. Various classes of cleaner energy sources such as wind energy, solar power, and sea tides were explored, and continuous and controlled supply of energy from these sources requires the development and growth of devices meant for energy conversion and storage. Electrochemical energy storage is the most suitable technology for energy conversion and storage due to high theoretical efficiency of converting chemical energy to electrical energy. The energy storage process at electrode surfaces involves different phenomena due to the distinctive nature of the electrode and electrolyte interactions. Generally, three types of interaction occur on the electrode surface between the electrode and electrolyte known as (1) EDLC, (2) surface redox, and (3) intercalation of ions. Surface redox and intercalation are followed by the faradic law because of charge transformation reaction involved in the energy storage mechanism. Surface absorption, surface redox, and intercalation are responsible for pseudocapacitance and involve thermodynamic and kinetic behavior of electro-sorption/desorption. Interaction of species on the electrode surface is via either attraction or repulsion; surface attraction (redox) is followed by Langmuir electrosorption (sharp peak in the cyclic voltammetry curve) and repulsion (peak broadening) is followed by Frumkin electrosorption (broad peak in the cyclic voltammetry curve). RuO\textsubscript{2} was the first reported material to show pseudocapacitive charge storage behavior. According to the charge storage mechanism, pseudocapacitors have access to different oxidation states for redox charge transfer that can enable higher energy density compared...
To increase higher energy density, an asymmetry cell shows better performance when the capacitor component stores electrochemical energy by electrostatic force, and the battery component enhances the electron transfer in the hybrid electrode system, which leads to better charge transfer reaction at high current rates. Many studies are being carried out on transition metal oxide-based materials such as NiO, V_{2}O_{5}, spinel Co_{3}O_{4}, Fe_{2}O_{3}, and mixed spinel NiCo_{2}O_{4} to explore electrodes for the pseudocapacitor. However, structural instability and performance degradation issues related to transition metal oxide lead to investigation of the novel framework structure for higher surface charge storage and better structural stability. Metal-organic frameworks (MOFs) are used as an interesting open framework structure, where materials are constructed by joining metal-containing units with organic linkers, generating an interesting three-dimensional structure.

Figure 1. (a) XRD pattern of Ni_{0.5}Co_{0.5}C_{2}O_{4}·2H_{2}O and Ni_{0.5}Co_{0.5}C_{2}O_{4}, (b) Rietveld refinement of the XRD profile of anhydrous Ni_{0.5}Co_{0.5}C_{2}O_{4} (vista image in the inset), (c) TGA of Ni_{0.5}Co_{0.5}C_{2}O_{4}·2H_{2}O in a N_{2} atmosphere (inset shows the DTA plot), (d) FT-IR spectra of Ni_{0.5}Co_{0.5}C_{2}O_{4}·2H_{2}O and Ni_{0.5}Co_{0.5}C_{2}O_{4}, and (e) BET surface area measurement plot of Ni_{0.5}Co_{0.5}C_{2}O_{4}·2H_{2}O and Ni_{0.5}Co_{0.5}C_{2}O_{4}.
dimensional or two-dimensional network with permanent porosity. Highly porous metal–organic framework structures, especially utilizing an oxalate linker with active participation metal ion redox, are known to show faradic pseudocapacitive characteristics. However, most of the oxalate materials have a high open structural space to accommodate the hydration of water, and that is why, most of the transition metal oxalates contain a structural water molecule. We have envisaged the controlled removal of structural water from the material to develop a novel porous structure that can accommodate a high degree of charge or anion intercalation/deintercalation couple with double layer capacitance to achieve superior capacitance. The controlled water removal can maintain the high porosity of the structure that can enable fast charge/ion transfer.

Here, in this article, we present the synthesis, characterizations, and electrochemical performances of hydrated Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O and porous anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ electrodes. The porous anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ electrode shows the specific capacitance value of 2396 F/g at 1 A/g, whereas hydrated Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O shows the capacitance equivalent to 810 F/g at 1 A/g in an aqueous 2 M KOH electrolyte. Furthermore, we assembled aqueous asymmetric supercapacitors (ASCs), in which porous anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ was used as the positive electrode and activated carbon (AC) was utilized as the negative electrode. Highest specific energy equivalent to 283 W h/kg were achieved at 1 A/g current rates by the combination of porous anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ and AC with high cyclic stability.

### EXPERIMENTAL SECTION

#### Synthesis

Synthesis of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O was carried out by the precipitation method. Highly porous anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ was prepared in two steps synthesis. 1.49 g of cobalt(II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O) and 1.46 g of nickel(II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) were dissolved in 200 mL of deionized water with continuous stirring using a hot plate magnetic stirrer, and 1.27 g of oxalic acid dehydrate (H$_2$C$_2$O$_4$·2H$_2$O) was added in solution. The entire mixture was stirred vigorously at 80 °C for 5 h. After 5 h of stirring, a white color precipitate of product Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O was obtained. The obtained product is then washed several times with deionized water. Finally, the washed product, Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O, was dried in a hot air oven at 90 °C for overnight. Porous anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ was formed after heating the material at 230 °C for 5 h in a N$_2$ atmosphere.

\[
\begin{align*}
\text{Co(NO}_3)_2\cdot 6\text{H}_2\text{O} + \text{Ni(NO}_3)_2\cdot 6\text{H}_2\text{O} &\quad + 2\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O} \\
&\quad \rightarrow 2\text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O} \downarrow + 2\text{HNO}_3 + 4\text{H}_2\text{O} \text{ at } 80 \degree C \\
\text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O} &\quad \rightarrow \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} \uparrow \text{ at } 230 \degree C
\end{align*}
\]

#### Characterizations

The crystal structure and phase purity of synthesized products were characterized through a Rigaku Miniflex desktop X-ray diffractometer (XRD) with Cu-Kα radiation (λ = 0.154 nm) in the range of 2θ = 10–90° with a step size of 0.02°. Xpert High Score (PANanalytical) software was used to identify the required phase. FE-SEM (FP 5022/22) was used to determine the surface morphology and structure of the sample. Infrared spectra of the samples were recorded using a Nicolet i55 FTIR spectrometer in the range of 400–4000 cm$^{-1}$. Pore size distribution and specific surface area of the sample were measured by BET (MicrotracBEL). All electrochemical performances of the sample including cyclic voltammetry (CV), galvanostatic charge discharge (GCD), and electrochemical impedance spectroscopy (EIS) were conducted using a conventional three-electrode arrangement measured by Metrohm Autolab (PGSTAT204) equipped with a FRA32M module. Electrochemical measurements were analyzed using NOVA1.1 software.

#### Preparation of Electrode

Hydrated Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O and anhydrous porous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ working electrodes were prepared in a 7:2:1 ratio of the active material, activated carbon, and binder (PVDF) in NMP solvent. Homogenous slurry was prepared using a mortar, and slurry containing ~1 mg of active materials was cast over a 1 cm$^2$ area of Torrey carbon paper. The coated electrode was dried at 80 °C for 12 h. The electrode loading was calculated through taking the weight of the electrode using an electronic balance (error limit: 0.01 mg). For that, the weight of Torrey paper was taken first, and then, the weight of the coated electrode (after drying the coated ink on Torrey carbon paper on 1 × 1 cm$^2$ area) was taken for the study. Then, from the difference in the weight, the exact loading of the electrode material was calculated.

### RESULTS AND DISCUSSION

The XRD peak pattern of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O and anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ powder confirms the phase purity and formation of the single phase material. Figure 1a shows the XRD plot of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O and anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ in the 2θ range of 10–60° with a step size of 0.02°. The prominent sharp diffraction peaks at 18.84, 22.78, 30.35, 35.6, and 49.08 represent the (202), (004), (400), (022), and (006) planes of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O in the orthorhombic cell (space group: Ccmm) and matches very well with the diffraction pattern of NiC$_2$O$_4$·2H$_2$O (JCPDS no. 25-0582). After annealing at 230 °C for 5 h, Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O transformed into anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$, which corresponds to the removal of structural water leaving the structure at 219°C. DTA shown in the inset clearly shows the loss of 35% was observed for decomposition of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$. That is why, to perform the control dehydration of materials, TGA was used to understand the thermal stability of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O. The first weight loss occurred at the temperature from 100 to 300 °C, which corresponds to the removal of structural water from the sample; in this temperature range, phase transformation also occurred from orthorhombic to monoclinic. The TGA curve determines the weight loss of 27%, as 2 mol of water was removed from the sample in the temperature range of 100–300 °C. DTA shown in the inset clearly shows structure water leaving the structure at 219 °C, and the second weight loss step or decomposition of the oxalate group occurs in the temperature range of 350–500 °C, in which the weight loss of 35% was observed for decomposition of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$. That is, to perform the control dehydration of materials, the phase purity of the sample was confirmed.
we carried out dehydration or annealing at 230 °C to avoid rapid loss of structure water that can damage the porous structure and can result in particle segregation. Thus, to protect the porous structure of the anhydrated materials, annealing was carried out at 230 °C in a N₂ atmosphere. Weight loss steps can be represented as follows

\[ \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} \quad (T \sim 200 ^\circ \text{C}) \]

\[ \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 \rightarrow \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 + \text{CO} + \text{CO}_2 \quad (T \geq 450 ^\circ \text{C}) \]

FTIR spectra of \( \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \) and anhydrous \( \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 \) powder samples shown in Figure 1d reveal the presence of different functional groups in the material. The broad peak at 3381.71 cm\(^{-1}\) belongs to the stretching vibration of the hydroxyl group (−OH), which signifies the presence of water in \( \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \). The observed peak at 1620.75 cm\(^{-1}\) was assigned to the antisymmetric carbonyl stretching band (C=O) specific to the oxalate group. Two weak peaks at 1326.86 and 1310.75 cm\(^{-1}\) were attributed to vibrations of \( \text{C}_2\text{O}_4^{2-} \) (C−O) and (C−C) and (C−O) + (O−C=O), respectively. The peak at 829.16 cm\(^{-1}\) was assigned to the vibration mode of \( \text{C}_2\text{O}_4^{2-} \) and O−C=O bending vibrations (O−C=O). The absorption peak at 478.19 cm\(^{-1}\) can be attributed to both Ni−O and Co−O bonding present in the prepared sample of Cobalt oxalate dehydrate (\( \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \)). The annealing product after structural water removal represents \( \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 \). The FT-IR study clearly shows the distinctive decrease in peak intensity of stretching vibration of the hydroxyl group (−OH) near 3381.73 cm\(^{-1}\). Figure 1e shows the BET results of the \( \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 \) sample. The nitrogen adsorption and desorption isotherm shows characteristics, which corresponds to the mesoporous structure of the oxalate; \( \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 \) sample. The calculated BET specific surface area and average pore diameter is 129.82 cm\(^2\)/g and both micropores and mesopores with diameters of 1.5−3.92 nm, respectively. Mesoporous structures attribute to excellent...
electrochemical kinetics due to high porosity. The calculated pore diameter of the Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ sample is much higher than that of the ions present in aqueous electrolytes.$^{28,29}$

Figure 2a shows the X-ray photoelectron spectroscopy (XPS) survey plot of the Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ sample, further confirming the presence of Ni and Co in the material. The Ni (2p) spectrum shown in Figure 2b could be assigned to 2p$_{3/2}$ of Ni$^{2+}$ (854.12 eV) and 2p$_{1/2}$ of Ni$^{2+}$ (871.71 eV) ions, as well as the corresponding satellite peaks at 859.83 and 876.71 eV. The Co (2p) spectrum shown in Figure 2c could be divided into peaks, which can be assigned to 2p$_{3/2}$ of Co$^{2+}$ (779.11 eV) ions, as well as the corresponding satellite peaks at 783.87 and 799.87 eV that arise from Co$^{2+}$ ions. The O(1s) spectra shown in Figure 2d corresponds to binding energies at 530.23 and 528.58 eV for Ni$^{2+}$ (854.12 eV) and 2p$_{1/2}$ of Ni$^{2+}$ (871.71 eV) ions, as well as the corresponding satellite peaks at 783.87 and 799.87 eV that arise from Co$^{2+}$ ions. The O(1s) spectra shown in Figure 2d could be divided into peaks, which can be assigned to 2p$_{3/2}$ of Ni$^{2+}$ (854.12 eV) and 2p$_{1/2}$ of Ni$^{2+}$ (871.71 eV) ions, as well as the corresponding satellite peaks at 783.87 and 799.87 eV that arise from Co$^{2+}$ ions.

Electrochemical Studies. Electrochemical performance of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O and porous anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ as the working electrode was characterized using a three-electrode system, where Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O and porous anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ act as working electrodes, saturated Hg/HgO (1 M KOH) as a reference electrode, and a platinum wire as a counter electrode in 2 M KOH as an electrolyte. The charge storage behavior of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O and porous anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ was characterized using cyclic voltammetry (CV) curves in the potential range of 0–0.6 V. Figure 4a represents the CV curve of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O. The nature of the curve explains the pseudocapacitive behavior coupled with surface redox (electrosorption). The CV curve of highly porous anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ shown in Figure 4b shows that pseudocapacitive storage followed intercalation association with surface redox. Redox peaks are originated due to the reversible transformation between Co$^{2+}$ to Co$^{3+}$ and Ni$^{2+}$ to Ni$^{3+}$ through electrosorption (redox) of OH$^-$ ions.$^{31}$

$$2\text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 + 2\text{OH}^- \leftrightarrow \text{Ni}_{0.5}\text{Co}_{0.5}\text{C}_2\text{O}_4 + 2\text{OH}^- + 2e^-$$

From the CV curve, specific capacitance $C$ (F/g) can also be calculated as one of the significant parameters to understand the electrochemical performance of the working electrode.

$$C_{sp} = \frac{\int i (V) dV}{mV^2}$$

where “m” is the mass of active material in the electrode (g), “V” is the potential window (V), and “$\theta$” is the scan rate (mV/s).

The specific capacitances of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O and anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ were calculated using eq 6, and capacitance was found to be close to 671 and 1993 F/g at 1 mV/s, respectively. The highly porous anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ attains higher charge storage, resulting in much higher capacity compared to hydrated Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O. In the voltage window of 0.6 V, the theoretical capacity of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O and anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ will be 879.55 F/g and 1096 F/g, respectively, with 1e$^-$/OH$^-$ charge transfer coupled with reversible intercalation/de-intercalation of OH$^-$ ions. This suggests that there is at least transfer/exchange of 0/76e$^-$/OH$^-$ per Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O and 1.82 e$^-$/OH$^-$ per Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ molecule, suggesting participation of both Ni$^{2+/3+}$ and Co$^{2+/3+}$ redox couples in charge storage. The redox reaction for high capacitance of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O can be represented as

$$\text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 + 2\text{OH}^- + 0.76\text{OH}^- \leftrightarrow \text{Co}_{0.5}\text{Ni}_{0.5}\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$$

As given in eq 8, the capacitance of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ can be represented as a combination of redox reaction as well as double layer formation as electron transfer is more than 1.
The value of $x$ can vary with scan rates, and the detailed electrochemistry Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ is described later to understand the charge storage mechanism of the electrode. We believe that as Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ can easily accommodate two structural water molecule to form Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O, the anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ accommodate high charge transfer ($1.82e^-$/OH$^-$) coupled with double layer capacitance formation to result in very high capacity for the anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ electrode.

Figure 4c shows a comparative plot of the CV curve of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O and Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ at a scan rate of 10 mV/s. The plot clearly reveals that there are two different types of redox phenomena occurring in the charge storage process; Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$·2H$_2$O follows surface redox and Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ surface redox with intercalation and double layer formation.

As the anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ electrode showed much superior pseudocapacitive storage, we focused our study mainly on the anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ only. Figure 4d shows the linear relation between anodic and cathodic peak current with respect to square root of scan rate and indicates that anhydrous Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ undergoes the semi-infinite diffusion-controlled process. Furthermore, kinetics of the electrode can be understood by determining the diffusion coefficient. The diffusion coefficient for the electrode was determined using the Randles–Sevick equation.

$$i_p = 2.686 \times 10^5 \times n^{3/2}AD^{1/2}C_0^{1/2}$$

(9)

where $i_p$ is peak current (A), $n$ is the number of electrons transferred in the redox event (usually 1), $A$ is the electrode area in cm$^2$, $D$ is the diffusion coefficient in cm$^2$/s, $C_0$ is the OH$^-$ ion concentration in mol/cm$^3$, and $\nu$ is the scan rate in V/s. According to the equation, the diffusion coefficient of Co$_{0.5}$Ni$_{0.5}$C$_2$O$_4$ were calculated to be $1.916 \times 10^{-11}$ cm$^2$/s for oxidation and $4.8931 \times 10^{-11}$ cm$^2$/s for reduction.
To further estimate the qualitative contribution of the different charge storage kinetics/mechanisms of the electrode, the power law equation given in eq 10 was utilized.

$$i = a
\nu^b$$

where $a$ and $b$ are adjustable values, $i$ is the current (A), and $\nu$ is the scan rate (V/s). The value of $b$ lies between 0.5 and 1; $b = 0.5$ stands for the semi-infinite diffusion control reaction, that is, battery type intercalative behavior, while $b = 1$ stands for the capacitive behavior.

**Figure 5.** Electrodynamic characteristics of the Ni$_{0.5}$Co$_{0.5}$C$_2$O$_4$ electrode; (a) plot of the linear relationship between log (peak current) and log (scan rate) at two different scan rate regions, (b) plot of power law of the charged state at a potential and discharged state at a potential, (c) contribution of diffusive and capacitive contribution at different scan rates, (d) analysis of kinetic contribution at 10 mV/s, and (e,f) Trasatti plot at different scan rates.
for the surface control reaction or electrosorption. Figure 5a shows the slopes ($b$ value) of the corresponding log [peak current ($i_p$) versus log($v$)] plots. The $b$-values of oxidative and reductive current were found to be 0.58 and 0.57, respectively, indicating the dominance of semi-infinite diffusion-controlled intercalative processes resulting in battery-type supercapacitor behavior during the electrochemical reaction. \(35\)

Figure 5b shows the voltammetry sweep rate dependence that can distinguish quantitatively the capacitive contribution to the current response. The current response at a fixed

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**Figure 6.** (a) Charge/discharge curve of Ni$_{0.5}$Co$_{0.5}$C$_2$O$_4$·2H$_2$O, (b) charge/charge curve of porous anhydrous Ni$_{0.5}$Co$_{0.5}$C$_2$O$_4$, (c) capacitance performance of porous anhydrous Ni$_{0.5}$Co$_{0.5}$C$_2$O$_4$ at different constant current rates, (d) capacitance retention and Coulombic efficiency porous anhydrous Ni$_{0.5}$Co$_{0.5}$C$_2$O$_4$, and (e) EIS plot and enlarged (zoom) view of the EIS plot of Ni$_{0.5}$Co$_{0.5}$C$_2$O$_4$·2H$_2$O and porous anhydrous Ni$_{0.5}$Co$_{0.5}$C$_2$O$_4$ electrode at 10 mV (AC).
potential is the contribution of two separate mechanisms, surface capacitive effects, and diffusion-controlled insertion or intercalation.

\[ i(u) = k_1 \mu + k_2 \mu^{1/2} \]  \hspace{1cm} (11)

For better understanding, eq 11 was modified as

\[ \frac{i(v)}{v^{1/2}} = k_1 + k_2 \]  \hspace{1cm} (12)
In eq 11, \( k_1 \) and \( k_2 \) represent the current contributions from the surface capacitive process and the diffusion-controlled intercalation process, respectively. Thus, after determination of \( k_1 \) and \( k_2 \), we can quantify their contribution in the current density at specific potentials. \(^{36} k_1 \) and \( k_2 \) were determined from obtaining the slope and intercept of \( y \) axis from linear fit. The representative curve \( (i(V)/\nu)^{1/2} vs \nu^{1/2} \) shown in Figure 5c represents the contribution of surface capacitivity and diffusion-controlled intercalation at different scan rates. Figure 5d represents specific contribution at a 10 mV/s scan rate, and contribution of surface capacitance or electrosorption was found to be 58% and that of diffusion-controlled intercalation was found to be close to 42%.

According to Trassati, the total specific capacitance is the sum of inner and outer surface capacitance of the electrode. It can be expressed as

\[
C_{\text{total}} = C_{\text{in}} + C_{\text{out}} \quad (\text{F/g})
\]

The specific capacitance contributed from the inner and outer surface of the electrode is dependent on scan rate.\(^{37} \) Figure 5e shows the linear fit \( C^{-1} \) versus \( \nu^{1/2} \) at different scan rates, and the \( y \)-intercept represents the amount of total charge storage or capacitance of the electrode. Figure 5f shows the linear fit \( C \) versus \( \nu^{1/2} \), and the \( y \)-intercept represents the outer surface charge storage or capacitance of the electrode. After calculating the \( y \)-intercept value applied on the Trassati plot, the total capacitance value \( (C_{\text{total}}) \) was found to be 1993 F/g. \( C_{\text{in}} \) was found to be 754 F/g (38% of the total capacitance value), and \( C_{\text{out}} \) was found to be 1239 F/g (62% of the total capacitance value).

Galvanostatic experiments were carried out to get more accurate capacity assessment of Co$_{0.5}$Ni$_{0.5}$CO$_4$ and highly porous anhydrous Co$_{0.5}$Ni$_{0.5}$CO$_4$.2H$_2$O electrodes. From the charge/discharge curve, the specific capacitance of the electrode was calculated using eq 14.\(^{32} \)

\[
C_p = \frac{I \Delta t}{m \Delta V}
\]

where \( I \) is the discharge current (A), \( \Delta t \) is the discharge time (s), \( m \) is the mass of the active material in the electrode (g), and \( \Delta V \) is the potential change during discharge (V). Figure 6a depicts the specific capacitances of Co$_{0.5}$Ni$_{0.5}$CO$_4$2H$_2$O and the values were found to be 810, 350, and 216 F/g at current densities of 1, 2, and 5A/g, respectively. Figure 6b shows the specific capacitances of the highly porous anhydrous Co$_{0.5}$Ni$_{0.5}$CO$_4$ electrode, and the values were found to be 2409, 2396, 2126, 1226, and 1083 F/g at current densities of 0.5, 1, 2, 5, and 10 A/g, respectively.

It has been observed that with increase in current density, there was decrease in specific capacitance of the electrode. In the desired range of current density, the specific capacitance decreases to 55% of its initial value. Figure 6c shows the capacitance value of the cycle number with different currents of the highly porous anhydrous Co$_{0.5}$Ni$_{0.5}$CO$_4$ electrode. Figure 6d exhibits the excellent long-term cyclic stability of highly porous anhydrous Co$_{0.5}$Ni$_{0.5}$CO$_4$ electrodes at 10 A/g for 5000 cycles. 87% capacity retention reflects that the specific capacitance of the electrode did not change much from the initial capacitance after 5000 cycles. The columbic efficiency (\( \eta = t_d/t_f \)) of the electrode was 94.8% after 5000 cycles of charge/discharge, which reveals the high reversibility of the highly porous anhydrous Co$_{0.5}$Ni$_{0.5}$CO$_4$ electrode. In addition to electrochemical stability, we performed AC electrochemical impedance spectroscopy (EIS) at 10 mV, as shown in the Nyquist plot in Figure 6e, in the frequency range of 1 MHz to 0.1 Hz. The specific impedance contribution was attributed to the impedance distributions over electric series resistance (\( R_s \)), charge transfer resistance (\( R_{ct} \)), and Warburg impedance (\( R_w \)). Higher frequency resistance was found for Co$_{0.5}$Ni$_{0.5}$CO$_4$2H$_2$O than porous anhydrous Co$_{0.5}$Ni$_{0.5}$CO$_4$ electrodes, as the intercept of the EIS spectra on the real axis was found to be at 1.43 and 0.8 Ω, respectively, indicating very small internal resistance for the anhydrous Co$_{0.5}$Ni$_{0.5}$CO$_4$ electrode. The small semicircle in the high frequency region shows the fast charge transport between the electrode and electrolyte. Lower frequency data represent the Warburg diffusion resistance for the samples. The straight line in the low frequency region for the porous anhydrous CO$_{0.5}$Ni$_{0.5}$CO$_4$ electrode is close to a 90° angle [very close to −Z’(Ω) axis], and the horizontal line represents the characteristic of more pseudocapacitance behavior of the electrode. The straight line in the low frequency region also represents fast OH− ion diffusion in the porous structure.\(^{38} \)

**Two Electrode Test.** To understand the real charge storage behavior of the porous anhydrous Co$_{0.5}$Ni$_{0.5}$CO$_4$ sample relative to AC (activated carbon), two electrode measurements have been conducted in 2 M KOH. To determine the maximum specific capacitance during the full test, storage capacity of positive and negative electrodes needs to be balanced as per the following equation

\[
\frac{1}{C_{\text{total}}} = \frac{1}{C_{\text{positive}}} + \frac{1}{C_{\text{negative}}}
\]

For balancing the charge storage capacity of the cell, the mass ratio \( (m^+ / m^-) \) of positive and negative electrode material was measured using the following equation

\[
\frac{m^+}{m^-} = \frac{C_- \times \Delta E_-}{C_+ \times \Delta E_+}
\]

where \( m^+ \), \( m^- \), \( C_+ \), \( C_- \), \( \Delta E_+ \), and \( \Delta E_- \) are mass, specific capacitance, and potential window of positive and negative electrodes estimated by three-electrode measurement, respectively.\(^{39,40} \)

Figure 7a shows CV curves at a 10 mV/s scan rate, where AC (activated carbon) was used as the negative electrode and porous anhydrous Co$_{0.5}$Ni$_{0.5}$CO$_4$ was used as the positive electrode. The calculated mass ratio \( (m^+/m^-) \) was found to be 1:5.3 for the symmetric cell, and the weight of the active material was measured to be 4.41 mg (excluding the weight of acetylene black and PVD). Figure 7b demonstrates the CV curve of porous anhydrous Co$_{0.5}$Ni$_{0.5}$CO$_4$/AC two-electrode ASCs [asymmetry supercapacitor cell at scan rates of 1–100 mV/s in this potential window (1.6 V)]. Figure 7c subsequently shows the galvanostatic charge/discharge curve, and the capacitance values were calculated by eq 13. Capacitance values were found to be 796, 515, 453, 421, and 211 F/g at current densities of 1, 2, 3, 5, and 10 A/g, respectively. Figure 7d shows the EIS plot (Nyquist) in the frequency range of 1 MHz to 0.1 Hz at 10 mV/s, confirming the retention of the electronic structure and resistance of the full cell (anhydrous Co$_{0.5}$Ni$_{0.5}$CO$_4$/AC), as impedance of the material decreases after completion of 2500 cycles compared to the first cycle. Figure 7e shows the columbic efficiency of the two-electrode cell, and the cell has lost only 3% efficiency after completion of 2500 cycles with higher capacity retention (90.7%) of its initial value after 2500 cycles. Specific energy
and specific power of asymmetric capacitors were calculated using the following equations

\[
E(W/h/kg) = \frac{C_{ASC} \times V^2}{2 \times 3.6}
\]  
\[
P(W/kg) = \frac{E \times 3600}{t_{dis}}
\]

where \(C_{ASC}\) is specific capacitance, \(V\) is operating voltage and \(t_{dis}\) is discharge time. 40

Figure 7f shows the plot of specific energy versus specific power with different constant current rates. Resultant values confirm the highest specific energy equivalent to 283 W h/kg at 1 A/g current density with specific power equivalent to ~817 W/kg. The maximum specific power of ~7981 W/kg was obtained when specific energy reduced to ~75.37 W h/kg at 10 A/g of current density. The capacitances of bulk/pristine transition-metal oxalate-based pseudocapacitors are summarized in Table 1 and are similar to those of anhydrous Co0.5Ni0.5C2O4 electrodes. The charge storage pseudocapacitive behavior of the Co0.5Ni0.5C2O4 electrode and the capacitance value are comparable or superior to that of most of bulk/pristine transition-metal oxalate-based pseudocapacitors reported to date. 29,41-44

We believe that the control release of the water molecule from hydrated transition oxalate molecule results in anhydrous porous structured material that can accommodate storage of two molecules/ions (OH\(^{-}\)) (intercalation couple with double layer capacitance) over the electrode is the key step in developing superior capacitance or charge storage materials. 45

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**CONCLUSIONS**

In summary, porous anhydrous Co0.5Ni0.5C2O4 was successfully synthesized using a two-step process; first, Co0.5Ni0.5C2O4·2H2O was synthesized by the co-precipitation method in aqueous medium, and then Co0.5Ni0.5C2O4·2H2O was heated at 230 °C for 5 h, which resulted in porous anhydrous Co0.5Ni0.5C2O4. The anhydrous Co0.5Ni0.5C2O4 electrode showed a highly pseudocapacitive performance with a specific capacitance of 2396 F/g at a current density of 1 A/g and excellent cyclic stability. Predominant intercalative mechanism seems to operate behind high charge storage capacity of the materials as intercalative (inner) and surface (outer) charges stored by porous anhydrous Co0.5Ni0.5C2O4 were close to high 38 and 62%, respectively. The porous anhydrous Co0.5Ni0.5C2O4/AC full cell resulted in 283 W h/kg of maximum specific energy with a specific power equivalent to 817 W/kg in the voltage window of 1.6 V in the 2 M KOH electrolyte at 1 A/g current rate. These results confirm that porous anhydrous Co0.5Ni0.5C2O4 can act as a potential pseudocapacitive electrode for large-scale energy storage application.

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