Inhibition of Redox Behaviors in Hierarchically Structured Manganese Cobalt Phosphate Supercapacitor Performance by Surface Trivalent Cations

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§Supporting Information

ABSTRACT: The stability and performance of supercapacitor devices are limited by the diffusion-controlled redox process occurring at materials’ surfaces. Phosphate-based metal oxides could be effectively used as pseudocapacitors because of their polar nature. However, electrochemical energy storage applications of Mn–Co–based phosphate materials and their related kinetics studies have been rarely reported. In this work, we have reported a morphology-tuned MnCo3−x(PO4)2·8H2O (MCP) spinel compound synthesized by a one-step hydrothermal method. Detailed physical and chemical insights of the active material coated on the nickel substrate are examined by X-ray diffraction, field-emission scanning electron microscopy, field-emission transmission electron microscopy, and high-resolution X-ray photoelectron spectroscopy analyses. Physiochemical studies reveal that the well-defined redox behavior usually observed in Co3+/Ni2+ surface-terminated compounds is suppressed by reducing the davalent cation density with an increased Co3+ and Mn3+ surface states. A uniform and dense leaflike morphology observed in the MnCo3 phosphate compound with an increased surface area enhances the electrochemical energy storage performance. The high polar nature of P–O bonding formed at the surface leads to a higher rate of polarization and a very low relaxation time, resulting in a perfect square-shaped cyclic voltammetry and triangular-shaped galvanostatic charge and discharge curve. We have achieved a highly pseudocapacitive MCP, and it can be used as a vital candidate in supercapacitor energy storage applications.

INTRODUCTION

Inadequate nonrenewable energy resources and a huge upsurge in environmental pollution urges us to find some ultimate clean and efficient energy storage devices such as batteries and supercapacitors (SCs) to be used in electric vehicles to replace gasoline fuels. Though both batteries and SCs rely on the electrochemical process, the charge storage mechanisms in batteries arise from the intercalation/de-intercalation of ions (Faradaic process) into bulk cathode materials and are slow diffusion-controlled charge transfer kinetic processes because of active mass transport,1,2 whereas in SCs, charge storage arises from electric double-layer capacitors (EDLCs), which is a non-Faradaic process.3,4 because of the polarization of the charges at the electrode/electrolyte interface, it does not depend on redox reactions and hence show fast response to the changes in the potential without any diffusion limitations, and it excel high power outputs; however, it has low energy density because the charge storage is confined only at the surface of the electrodes.3–5 Mostly, activated porous carbon-based materials used as SCs, possess high specific capacitance because of high surface charge density stored electrostatically and very short charge separation distance (1 nm) at the electrode/electrolyte interface and hence show a very high time rate of polarization.6–9 Recently, transition metal oxide-based materials are widely used as pseudocapacitors, where faradic reactions were accompanied by the EDLC, resulting in a high charge storage capacity,10–12 A perfect pseudocapacitive material (e.g., MnO2 and RuO2) gives a triangular charging/discharging profile and show a rectangular cyclic voltammery (CV) behavior.13,14 However, many of these materials show asymmetry in charging/discharging because of the energy loss associated with sluggish kinetics and diffusion-controlled transport.15–18 In this respect, phosphate-based metal oxides could be effectively used as pseudocapacitors because of the polarization originated from the polar nature of the materials. Even though very few transition metal phosphates such as Mn3(PO4)2,19 Co3(PO4)2,20 Co3P2O8,21 Ni(PO4),22 and VOPO423 were reported, the presence of redox peaks in the CV sweep and a
plateau in the charging/discharging profile limit their applications. Usually, Ni(OH)₂ and CoO₂ mostly show well-separated oxidation/reduction peaks (Faradaic) in the KOH electrolyte because of their low redox potential in divalent surface cations, which is a typical behavior of batteries.¹⁹⁻²⁴ Even though manganese phosphate and cobalt phosphate have been reported as pseudocapacitive materials, either the CV voltage has been swept from negative to positive or it shows oxidation/reduction behaviors.²⁵⁻²⁷ Hence, it is highly essential to alleviate the redox behaviors usually observed in metal phosphate-based materials and understand the electrochemical charge storage mechanisms based on their kinetics. Trivalent cations have very high redox potential and could be a solution to solve the above problems, which were not reported to the best of our knowledge. Here, we have reported a Mn−Co phosphate spinel compound having trivalent cation-terminated surfaces, which not only suppressed the redox behaviors but also enhanced the specific capacitance in the highly ordered hierarchically structured MnₓCo₃₋ₓ(PO₄)₂·8H₂O (MCP) deposited on nickel foam (NF) current collectors.

Scheme 1. Schematic Representation of the Synthesis Method of the Hierarchically Structured MCP Thin Films

**RESULTS AND DISCUSSION**

The synthesis process of the hierarchically structured MCP is illustrated in Scheme 1, and the samples are named as Mn₁₀Coₓ, Mn₁₀Co₃₋ₓ, Mn₉Co, and Mn₆Co for x = 0.5, 1, 1.5, and 2, respectively. X-ray diffraction (XRD) was performed to know the crystalline phase of the as-prepared MCP thin films deposited on NF. Figure 1 shows the XRD patterns of the as-prepared MCP films with various Mn concentrations such as Mn₉Co, Mn₁₀Co₁₋₅, MnCo, and Mn₆Co. The standard XRD patterns of MCP (ICCD no. 00-041-0375) and Mn₉₋₅(PO₄)₂·3H₂O (ICCD no. 00-003-0426) were used to match diffraction crystal planes of the deposited films. The diffraction patterns did not match with either Mn−PO₄ or Co−PO₄, but showed mixtures of both, ensuring the formation of compounds. When the Co atoms were replaced by Mn atoms in the monoclinic phase of Co₃(PO₄)₂·8H₂O, the structural morphology was rearranged because of the differences in ionic radii, bond lengths, and enthalpies of formation.²⁸

The formation of hierarchical structures depends on the ratio of the Mn/Co atomic concentration. Manganese has ionic radii of 81, 72, and 67 pm for Mn²⁺, Mn³⁺, and Mn⁴⁺ oxidation states, respectively, whereas cobalt has 79 and 68.5 pm for Co²⁺ and Co³⁺, respectively. To maintain charge neutrality, there are only two possible rearrangements between the ionic charge states of Mn²⁺/Co²⁺ and Mn³⁺/Co³⁺. XRD reveals that the crystallinity is very high for Mn₁₀Co (reduced cobalt concentration) and shows a monoclinic cobalt phosphate structure with increasing cobalt concentration (Mn₁₀Co₃₋ₓ). Figure 2 shows the field-emission scanning electron microscopy (FE-SEM) images of the as-prepared (a) Mn₉Co, (b) Mn₁₀Co, (c) MnCo, and (d) Mn₆Co phosphates. The hierarchically structured MCP thin films were well-grown on the surface of NF because NF itself acts as nucleation sites for the growth of nanostructures.²⁶

When the Mn concentration was very low (Mn₁₀Co₃₋ₓ), flowerlike nanostructures were formed and the flower density was increased in Mn₆Co. With further increase in the Mn atomic ratio, the flower nanostructures were diminished and hexagon structures progressively increased. It is because that the Mn−(PO₄)₂ phase usually possesses a sheet or 3D structures and the Co−(PO₄)₂ phase possesses nanoflower structures.²⁰,²¹ The structural formation was uniform and denser leaflike structures were formed for the Mn₉Co₂ compound. Moreover, the nanoflower structures were transformed to hexagons and formed thicker crystals having a less surface area and a high crystalline nature in the Mn₆Co compound, as shown in Figure 2d. This clearly evidences the transformation of the phase and morphology from one motif to another motif and supports our XRD measurement. The elemental compositions of MCP@NF hierarchical structures were examined by energy dispersive X-ray (EDX) mapping and are shown in the Supporting Information Figure S1 for the best performing (a) MnCo₂ and (b) Mn₁₀Co₁₋₅ thin films.
Figure 2. FE-SEM images of the as-prepared (a) Mn$_{0.5}$Co$_{2.5}$, (b) MnCo$_2$, (c) Mn$_{1.5}$Co$_{1.5}$, and (d) Mn$_2$Co phosphates.

Figure 3. Field-emission transmission electron microscopy (FE-TEM) images, high magnification images, and selected area electron diffraction (SAED) patterns for the as-prepared (a–c) Mn$_{0.5}$Co$_{2.5}$ and (d–f) Mn$_2$Co phosphates.

Figure 4. High-resolution core level XPS spectra of (a) Mn 2p and (b) Co 2p.
The EDX surface mapping spectrum clearly illustrates the homogeneous distribution of Mn, Co, O, and P elements on NF. Even though nickel composition was very low compared to Mn, Co, and P, the intensity and distribution indicate the oxidation of nickel; otherwise, nickel would not be present on the surface of the films. Moreover, the elemental mapping images reveal that the surface of the nanostructures contains mostly O and P elements. The nanoscale structures were analyzed by FE-TEM and are shown in Figure 3a (Mn$_{0.5}$Co$_{2.5}$) and 3d (Mn$_2$Co). It reveals that the hexagons were grown over flower structures. The high-magnification images and SAED patterns are given in Figure 3b,c (Mn$_{0.5}$Co$_{2.5}$) and Figure 3e,f (Mn$_2$Co). The interatomic distances were calculated from TEM-SAED and compared with the XRD data. The interatomic distances of Mn$_2$Co along the (1 3 0) plane have been found to be 0.405, 0.407, and 0.412 nm from XRD, TEM, and TEM-SAED measurements, respectively. The high-resolution X-ray photoelectron spectroscopy (HR-XPS) studies were conducted to investigate the influence of Mn/Co atomic ratios on the surface binding oxidation states and the elemental composition of hierarchal MCP@NF. The HR-XPS spectra were fitted with Gaussian–Lorentzian (30% Gaussian) functions and a Shirley-type background and are shown in Figure 4a,b for Mn 2p and Co 2p, respectively. 

Mn was deconvoluted into three oxidation states: Mn$^{2+}$ (640.6 eV), Mn$^{3+}$ (642.7 eV), and Mn$^{4+}$ (646.2 eV), showing the presence of a mixed valence state on the surface of the nanostructures. It is very interesting to note that the amount of the Mn$^{4+}$ state was reduced with increasing the Mn content, and Mn$^{3+}$ is maximum for MnCo$_2$. Likewise, the Co 2p$_{3/2}$ peak was deconvoluted into two different oxidation states: Co$^{2+}$ (779 eV) and Co$^{3+}$ (781.3 eV), and the two satellites peaks were located at 784.3 and 786.7 eV. The amount of the Co$^{2+}$ state was not affected by the Mn/Co ratio, whereas Co$^{3+}$ is maximum for MnCo$_2$ and reduced for both Mn$_2$Co and Mn$_{0.5}$Co$_{2.5}$. It implies that the Mn$^{3+}$/Co$^{3+}$ charge state decides the electrochemical performance because the Co$^{3+}$ charge density increases the electronic conductivity. The core-level spectra of P 2p were deconvoluted in two peaks by fixing the spin-orbital splitting at 0.87 eV and area ratio at 2:1 between 2p$_{3/2}$/2p$_{1/2}$, and the full width at half maximum was fixed for same oxidation states and is illustrated in Figure 5a.

The deconvoluted peaks located at 132.4, 134.1, and 135.25 eV were respectively assigned to the phosphates corresponding
(PO₄)³⁻, (PO₃)²⁻, and P₂O₅. The P₂O₅ peak is observed only for MnCo₂, and the (PO₄)³⁻ amount was not affected by the Mn/Co ratio. Moreover, the Ni 2p spectra given in Figure 5b confirm the oxidation of the nickel metal substrate, and the Ni 2P₃/2 peak of core-level spectra was deconvoluted into two peaks such as Ni²⁺ (854.9 eV) and Ni³⁺ (857.7 eV), respectively, and the two satellite peaks at 860.5 and 863 correspond to the vacancy of NiO (Ni²⁺) and NiOOH (Ni³⁺), respectively. It clearly shows that the amounts of Ni³⁺, Mn³⁺, and Co³⁺ are maximum for MnCo₂. Moreover, the cation charge state of X³⁺ (X = Mn, Co, and Ni) is vital to decide the electrochemical performance by enhancing the anion absorption at the electrode/electrolyte interface, and increasing Co³⁺/Ni³⁺ amounts usually increase the redox potential and conductivity of the active material.

Prior to fabricating the symmetric cells, single-electrode performances were tested using the SP-150 electrochemical workstation in a three-electrode configuration with the saturated calomel electrode (SCE) as the reference electrode. Figure 6 illustrates the performance of the half-cell prepared from hierarchal MCP@NF electrodes. The galvanostatic charge–discharge (GCD) for various Mn/Co ratios is given in Figure 6a at 2 A/g current rate, and Figure 6b shows the best performing MnCo₂ phosphates at various current densities. The nonlinear (not triangular) plateau in the voltage versus time sweep shows the pseudocapacitive property of MCP, which mostly occur where there is a resistive loss. The specific capacitance values were calculated from the GCD curves using the formula given below:

$$C = \frac{q}{V} = \frac{i \times dt}{m \times V}$$

where C is the gravimetric capacitance, q is the charge, V is the voltage, dt is the discharge time, and m is the mass of the active material.

Double-layer capacitance mainly depends on three parameters such as the electrode surface area, electrolyte composition, and potential field between the charges at the interface. All the studies were done with the best ion donating electrolyte (KOH), which is a very effective aqueous electrolyte because of its wide operating window up to 1.4 V and can readily give solvated ions when dissolved in an aqueous medium. The rate of polarization is decided by the surface charges present at the electrode/electrolyte interface. The compound MnCo₂ has a
higher specific capacitance value of 979.91 F/g at a current rate of 2 A/g and maintains a high value of 566.7 F/g at 6 A/g. As we have seen from the morphological studies, it has the highest surface area and vertically arranged leaves over the conductive NF. At a current rate of 2 A/g, the specific capacitances were 593.7 F/g, 765.4, and 485 F/g for Mn0.5Co2.5, Mn1.5Co1.5, and MnCo2, respectively. Both Mn0.5Co2.5 and MnCo2 have a large size crystal and a lesser surface area, and the electrostatic active sites for possible polarization were minimal and lead to a poor performance. The multilayered structure in the Mn2Co compound has the surface screening effect and the conductivity could be very low. Moreover, MnCo2 and Mn1.5Co1.5 compounds have increased Co3+ and Mn3+ states, which contribute more electrochemical interconversions and results in high electrochemical capacitive contribution. In addition, the redox behaviors usually observed in Ni and Co oxides are suppressed by the trivalent cationic effects because of high redox potential. The charge transfer kinetics was studied by electrochemical impedance spectroscopy (EIS). Figure 6c shows the EIS of MCP@NF. The equivalent series resistances ($R_s$), determined from the high-frequency real part of the impedance intercept, were 0.53, 0.99, 0.98, and 1.63 $\Omega$ for Mn0.5Co2.5, MnCo2, Mn1.5Co1.5, and MnCo2, respectively.34–37 The charge transfer resistances ($R_{ct}$) calculated from the Nyquist plots were 0.09, 0.08, 0.04, and 0.13 $\Omega$ for Mn0.5Co2.5, MnCo2, Mn1.5Co1.5, and MnCo2, respectively. Both MnCo2 and Mn1.5Co1.5 compounds have nearly equal electron spin resonance (ESR) in the high-frequency real part of the interface. The inset graph (Figure 7d) shows the impedance resonance (ESR), showing a conventional EIS behavior of a pseudocapacitive material.34 Mn1.5Co1.5 and MnCo2 have low ESR compared to the reported phosphate-based materials.26,38 Figure 6d shows the current density versus specific capacitance of MCP electrodes. Mn1.5Co1.5 and MnCo2 have higher pseudocapacitance output and could be used as a better pseudocapacitive material for SC energy storage applications.

The electrochemical performance of symmetry cells was carried out in 3 M KOH alkaline electrolyte. Figure 7a shows the CV curve of symmetric SCs for different Mn concentrations at 20 mV/s. It can be seen that MnCo2 and Mn1.5Co1.5 have a rectangular shape, whereas Mn0.5Co2.5 and MnCo2 show a diffusive behavior. The diffusive behavior mainly arises from Ni2+ and Co2+ because they are not available for the adsorption of electrolyte ions. The electrochemical capacitive contribution in pseudocapacitive materials usually arises from the adsorption of electrolyte ions affected by the chemical affinities of the solvated ions to the electrode surface and also the field strength of the electric double layer.39 In the pseudocapacitive process, both the formation of the Helmholtz double layer and fast surface Faradaic process enhance the capacitance. The formation of a two-dimensional monolayer or quasimonolayer of electrochemically reactive species causes a reversible process. Even though the NiO oxidation state is a hindrance to the pseudocapacitive performance, disappearance of the well-separated redox peaks in our case ensures the significance of our work.25,40–42 Moreover, the electrical conductivity mainly depends on the cation valence state and is higher for X3+ (X = Co and Mn) because of the improved electron transport.43 Hence, the MnCo2 compound with enriched Co3+ and Mn3+ surface charge density and larger surface area lead to good performance in pseudocapacitance. The presence of P-O3 along with the PO4 gives the possibility of more sites for attracting the solvated protons (K+’) and help the MnCo2 phosphate compound to perform well in symmetrical SCs.

### CONCLUSIONS

In summary, highly ordered MCP was grown on NF current collectors by a simple one-step hydrothermal synthesis. A binder-, polymer-, and carbon-free approach was used to fabricate the active material on NF to avoid its effects in pseudocapacitance devices. The morphology was tuned by controlling the Mn–Co atomic ratios. We have concluded that MnCo2 compound with a uniform leaflike morphology and larger surface area could be a better option for the pseudocapacitive materials. Also, we have found that the oxidation of nickel that occurs during hydrothermal synthesis hinders the electrochemical performance; however, this could be avoided with suitable trivalent cation substitution. Even though NF is a good platform for the growth of nanostructures, reduction of the nickel metal into NiO and NiOOH leads to the oxidation/reduction reaction and mass transfer during the electrochemical processes should be avoided.

### EXPERIMENTAL SECTION

#### Material Synthesis

All the chemicals were purchased from Sigma-Aldrich and used without further purification. Highly ordered hierarchal MCP nanostructures were grown on conductive NF substrates of thickness 0.2 mm. The NF was washed using 3 M HCl to remove the oxides, followed by acetone, ethanol, and finally DI water under ultrasonication prior to the deposition. An equimolar concentration of ammonium dihydrogen phosphate (NH4H2PO4), cobalt nitrate hexahydrate (Co(NO3)2·6H2O), and manganese nitrate tetrahydrate (Mn(NO3)·4H2O) was added to 100 mL of DI water, stirred vigorously at room temperature for 30 min, and then transferred to a Teflon-lined stainless-steel autoclave with the...
NF kept vertically at 120 °C for 8 h. Finally, the NF substrates were collected and washed with acetone, ethanol, and DI water. Four different molar ratios of MCP (x = 2, 1.5, 1, and 0.5) were used to tune the cobalt and manganese concentration, named respectively, Mn2Co, Mn1.5Co1.5, MnCo, and MnCo2 for ease of identification.

**Electrochemical Measurement.** For electrochemical measurement, MCP/NF electrodes were cut into 1 × 1 cm and used as a working electrode in a standard three-electrode cell configuration with a platinum wire and SCE as used as counter and reference electrodes. For a complete cell, symmetrical electrodes of Mn2Co, Mn1.5Co1.5, MnCo, and MnCo2 deposited on NF were assembled. The electrochemical measurements such as CV, EIS, and GCD were performed using BioLogic SP-150 electrochemical workstation in 3 M KOH alkaline electrolyte.

**Material Characterization.** The crystal structure was analyzed using a X-ray diffractometer (Bruker D-8 ADVANCE) with Cu Kα operated at 40 kV and 30 mA in the range of 10°–70°. The surface morphologies were analyzed using FE-SEM (Zeiss SUPRA 25) and FE-TEM (Talos F200X). Surface binding states and elemental compositional analysis were characterized by XPS using a Thermo Fisher Scientific (UK) ESCALAB 250 system with monochromatic Al Kα radiation at 1486.6 eV and with an electron take-off angle of 45°. The chamber pressure was kept below 10−10 Torr during the measurement. The survey spectrum was scanned in the binding energy (BE) range of 100–1200 eV in 1 eV steps and were calibrated using a fixed core-level peak of adventitious carbon (C 1s) at 284.6 eV as a reference. Peak fitting and quantitative analysis were done using the CasaXPS program (Casa Software Ltd), and the results were justified using an average matrix relative sensitivity factor with respect to the peak area and atomic sensitivity factor of the identified components. We used the lowest possible number of components to fit the data satisfactorily, and the uncertainty in the BE position was within 0.05 eV for a component.

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