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Interconnected Nanorods–Nanoflakes $Li_2Co_2(MoO_4)_3$ Framework Structure with Enhanced Electrochemical **Properties for Supercapacitors**

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The demand for sustainable energy to power new types of portable electronic has made the research for next-generation energy storage materials and devices extremely important. To overcome this crucial issue, supercapacitors that occupy an intermediate place between the traditional electrostatic capacitors and batteries in terms of power and energy density stand as a great opportunity. Electronic double-layer based supercapacitors (EDLCs) have proved high power density but at the expense of low energy density,^[1–5] while the other category known as pseudocapacitor exhibits fast charging-discharging and power density like EDLCs but displays a relative short lifetime. The pseudocapacitor undergoes the following accepted charge storage mechanisms: 1) electrolyte ions adsorption as a monolayer on the electrode surface, 2) fast redox reactions at the electrode-electrolyte interface, and 3) fast reversible intercalation/deintercalation of ions into the bulk of the material. All these mechanisms are expressed as capacitive charge storage or faradaic process,^[6–9] resulting in high energy density approaching that of batteries.

However, pseudocapacitive materials undergoing only ion adsorption and fast redox reaction display a limited energy density compared to batteries. To achieve this high energy density, bulk ion intercalation has attracted much attentions because it contributes with an extra capacitance and at some extend with enormously high capacitance.^[9] This mechanism needs materials with an appropriate structure, which can accommodate ion insertion without material destruction. In other words, the insertion reaction should be kinetically facile and the structural rearrangement does not occur during the electrochemical charge storage.^[10] Among materials, which can allow ion intercalation, layered transition metal oxides with large interlayer distance have been the most studied. Recently, Brezesinski et al.^[11] reported an extra contribution arising from ion intercalation occurring on the same timescale as redox pseudocapacitance into the van der Waals gaps of iso-oriented nanocrystalline α -MoO₃. In the same approach, Gogotsi and co-workers^[12]

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demonstrated a spontaneous intercalation of large range of cations into 2D MXenes layers providing an excess capacitance. Moreover, Mefford et al.^[8] reported an anion-based and oxygen intercalation charge storage mechanism for a nanostructured perovskite-type material. All these works indicate that an ion intercalation charge storage can occur through cation or anion intercalation in the bulk material. Besides, owing to the material destruction during the electrochemical process, low rate capability and cyclability remain a drawback to achieve practical application of pseudocapacitive materials. Thus, it is a challenge to find a pseudocapacitive material, which can simultaneously accommodate fast ion intercalation and sustain largecycle stability.

To overcome this challenge, materials with tunnel structure such as NASICON compound represent a big opportunity. Indeed, NASICON-type material with a typical chemical formula $Li_{v}M_{2}(XO_{4})_{3}$ with X = Mo, W, P, S, As and M = Co, Ni, Zr, Cd, so forth is a large family of compounds, which consist of clusters of MO₆ octahedra bridged by three-corner-sharing (XO₄) tetrahedral (Figure 1a). The octahedra of the clusters share corners with the tetrahedra of neighboring clusters to create an open 3D host crystal structure that allows easy diffusion of small-sized alkali cations.^[13-17] These 3D framework materials have been widely investigated for their high ion conductivity and present the advantage of accommodating large amount of ion to intercalate (until 5 per formula unit in Li case) without structure destruction.^[18]

To date, many NASICON-type compounds have been synthesized for use as membrane, fuel cells, and gas sensors.^[17] Although these materials mostly have been obtained by high temperature and harsh reaction conditions such as a solid-state reaction at 1000 °C, and widely investigated for energy storage (electrode for lithium-ion batteries).^[19] However, few reports have been made on its synthesis in mild condition with a morphology control, its pseudocapacitive behavior, and the mechanism supporting the high capacitance. In this work, the electrochemical performances of nanostructured Li₂Co₂(MoO₄)₃ 3D framework was investigated. Because NASICON-type compound is a large family, we believe that this work opens up to the exploration of vast number of high-capacity materials. Here, we report the synthesis of interconnected nanorods-nanoflakes Li₂Co₂(MoO₄)₃ 3D framework as pseudocapacitive material for supercapacitors. This electroactive material displays a remarkable capacitance retention of 67% (1055 to 700 F g^{-1} for an increase of current density from 1 to 50 A g^{-1}) and high cyclability of 91% capacity retention after 10 000 cycles at 30 A g^{-1}

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Figure 1. a) Schematic representation of the crystal structure of $Li_2Co_2(MoO_4)_3$, b) XRD spectra before and after annealed at various temperature, and c) TG and DTA curves of $Li_2Co_2(MoO_4)_3$.

in 2 M LiOH aqueous solution. The interconnected nanorods– nanoflakes morphology and the open 3D host crystal structure lead to the significant enhanced electrochemical performances.

The nanorods-nanoflakes $Li_2Co_2(MoO_4)_3$ was obtained by mild condition hydrothermal method and the microstructures are displayed in Figure 1b. The X-ray diffraction (XRD) patterns of the samples are consistent with the orthorhombic Li₂Co₂(MoO₄)₃ (JCPDS card No. 01-085-0059) with a Pnma space group and lattice parameters of a = 5.086 Å; b = 10.484 Å; and c = 17.606 Å. To obtain a better crystallinity, the as-prepared material was annealed at 350 °C, it can be seen that the XRD patterns became more resolved with the annealing process, which indicate an increase in the crystallinity due to the removal of water molecules. The thermal stability and dehydration processes are investigated by thermogravimetry-differential thermal analysis (TG-DTA). Figure 1c exhibits a typical thermogravimetric analysis (TGA) curve for Li₂Co₂(MoO₄)₃, the total weight lost during the whole process is about 6.4%. The weight loss is attributed to the removal of reversible bonded water molecules and water molecules forming the integral part of the crystal structure.^[20]

The as-prepared materials have been grown on a conductive substrate to avoid the use of a binder as it has a potential use as electrode for supercapacitor.^[21,22] The substrate also served as a current collector to provide fast electron transport. The schematic growth process of $Li_2Co_2(MoO_4)_3$ interconnected nanorods–nanoflakes is described in **Figure 2a**. To confirm this mechanism, we studied the morphology evolution versus the reaction time during the hydrothermal synthesis at 120 °C

and is proposed to be as follows: first the compound forms a seeds layer on the substrate to decrease the surface energy, second with an increase in time, oriented nanorods start to grow from the seeds, which served as the "growth spot,"^[23] third with a further increase of reaction time, nanoflakes start growing on previously formed Li₂Co₂(MoO₄)₃ nanorods. After around 12-14 h reaction, interconnected nanorods-nanoflakes are uniformly distributed on the substrate. Exceeding this reaction time, the nanorods-nanoflakes morphology is destroyed (Figure S2, Supporting Information). The experiment has been conducted on various substrates (3D nickel foam, carbon cloth, and carbon fiber paper (CFP)) and shows the same morphology for the final obtained product confirming that this material can be grown on different substrates (Figure S2, Supporting Information). It is also interesting to reveal that the nanorods-nanoflakes morphology grew on both sides of the substrate without the assistance of any other ion such as fluorine,^[24] and when the experiment was performed without a substrate, randomly sized rods were obtained as the final morphology.

Field-emission scanning electron microscopic (FESEM) and transmission electron microscopic (TEM) images depicted in Figure 2b–e show that the nanoflakes are well attached to the nanorods and no special fractures are observed between the two morphologies suggesting that nanoflakes grew onto nanorods and they are constituted of the same material. Furthermore, the high-resolution TEM images (insets Figure 2e) for individual nanorod and nanoflake of the sample annealed at 350 °C display an interplaner spacing of ca 0.447 nm indexed to the XRD peak corresponding to 19.8° according to the PDF card



Figure 2. a) Schematic illustration of the hydrothermal synthesis process of $Li_2Co_2(MOO_4)_3$ grown on conductive substrate. SEM and TEM images of $Li_2Co_2(MOO_4)_3$ before (b,c) and after annealed at 350 °C (d,e), respectively. The insets of (e) represent the HRTEM analysis of the nanoflakes (up inset) and the nanorods (bottom inset).

of Li₂Co₂(MoO₄)₃ (JCPDS card No. 01-085-0059), which confirm the similarity of the nanorods and nanoflakes. The morphology evolution versus annealing temperature has been studied through top-view FESEM images (Figure S3, Supporting Information). The interconnected nanorods–nanoflakes morphology was obtained for Li₂Co₂(MoO₄)₃ after hydrothermal synthesis and this morphology was kept after annealing at 350 °C with a decrease of the nanoflakes thickness. Moreover, when the annealing temperature increases from 450 °C to 600 °C, the nanorods–nanoflakes start to be destroyed, and then broken to short nanorods and finally agglomerate together. This phenomenon can be easily associated to the removal of water molecules as demonstrated by the TGA.

The electrochemical performances of the interconnected nanorods-nanoflakes Li₂Co₂(MoO₄)₃ were investigated through cyclic voltammetry (CV) and galvanostatic charge-discharge tests using a standard three-electrode electrochemical cell containing aqueous electrolytes. The CV measurements were carried out at various scan rates in the potential range between -0.1 and 0.5 V versus Ag/AgCl saturated calomel electrode (SCE). Figure 3a depicts CV curves of Li₂Co₂(MoO₄)₃ samples before and after annealing at 350 °C in 2 M LiOH electrolyte. Both samples show two anodic peaks at 0.2 and 0.3 V and two cathodic peaks at 0.05 and 0.18 V, respectively, constituting two redox couples, which indicate that the process is fully reversible. However, for both samples, the peaks positions did not change with the increase of the current density for slow sweep rate (0.1 to 10 mV s⁻¹) (Figure S4, Supporting Information) and the differences between anodic and cathodic peak voltage are 0.15 and 0.12 V, respectively, which indicate a pseudocapacitance behavior of the as-prepared electrode materials.^[25] As it can be observed from Figure 3a, the sample annealed at 350 °C displays an obvious increase in the surface area of the CV curve and more resolved redox peaks compared with its uncalcined counterpart. This phenomenon can be ascribed to the better crystallization and open tunnel after water removal, which easily allow ion

intercalation in the bulk material.^[26] When the CV tests were performed at sweep rate comprise between 50 and 500 mV s⁻¹, the anodic and cathodic peaks merge to a single broad couple of anodic and cathodic peaks, and shift noticeably with an increase in the peak separation, notwithstanding that, the capacity still reversible. According to the power-law relationship between current and sweep rate $(i = av^b)$, where a and b are adjustable values and a *b*-value of 0.5 would indicate that the current is controlled by linear diffusion, while a value of 1 indicates that the current is surface controlled.^[27,28] Plotting $\log(i)$ versus $\log(v)$ in range of 0.1 to 500 mV s⁻¹ (Figure 3b), the *b* factor exhibits a value for both anodic and cathodic current of 0.82 and 0.85 in 0.1 to 20 mV s⁻¹ and a value of 0.54 and 0.62 in 30 to 500 mV s⁻¹ sweep rates ranges, respectively. These values approaching 1 and 0.5 indicate that the kinetics are surface controlled and ion diffusion controlled in 0.1–20 and 30–500 mV s⁻¹ sweep rate intervals, respectively. Moreover, the CV test was conducted in different alkaline electrolytes (Figure S4, Supporting Information) at the same sweep rate. The CV curve obtained in Li-based electrolyte displays two couples of redox peaks, large surface area for the CV curves, and large potential window than those obtained in Na- and K-based electrolytes, which implied that the charge delivered by the intercalation/deintercalation of Li⁺ ion is higher than those of Na⁺ and K⁺ ions.^[29] Overall, the shape of the CV curves confirms that the as-synthesized material undergoes faradaic charge storage process in these electrolytes.

The galvanostatic charge–discharge measurements were conducted at different current densities from 1 to 50 A g⁻¹. The specific capacitance (C_s) can be calculated according to the following equation:

$$C_{\rm s} = \frac{2\int iV(t)\,\mathrm{d}t}{m\,\Delta\mathrm{V}^2} \tag{1}$$

where i is the discharge current, V is the voltage excluding the potential drop (IR), dt is the time differential, m is the loaded



Figure 3. a) CV graph at 10 mV s⁻¹ of $Li_2Co_2(MOQ_4)_3$ before and after calcination at 350 °C in LiOH electrolyte. b) Normalized peak-current plot to determine the *b*-value for anodic and cathodic process at scan rate from 1 to 500 mV s⁻¹ in LiOH electrolyte. c) Rate capability of $Li_2Co_2(MOQ_4)_3$ before and after calcination at 350 °C in LiOH electrolyte in current interval between 1 and 50 A g⁻¹. d) Rate capability of $Li_2Co_2(MOQ_4)_3$ annealed at 350 °C in LiOH, NaOH, and KOH electrolytes, respectively. e) Cycle performance of uncalcined and calacined $Li_2Co_2(MOQ_4)_3$ at 350 °C in LiOH electrolyte at 30 A g⁻¹. f) Nyquist plots of uncalcined and calacined $Li_2Co_2(MOQ_4)_3$ at 350 °C collected in LiOH, inset is the magnified view of the Nyquist plots in high-frequency region.

mass of the electroactive material, and ΔV is the potential window. The Li₂Co₂(MoO₄)₃ sample annealed at 350 °C shows the capacity varying from 1055 (1.03 F cm⁻²) to 700 F g⁻¹ (0.68 F cm^{-2}) from 1 to 50 A g⁻¹, (1 to 50 mA cm⁻²) corresponding to 67% capacity retention with a coulombic efficiency almost stable (98%-99.57%). Compared with the uncalcined counterpart (Figure 3c) that exhibits 57% capacity retention and coulombic efficiency varying from 90% to 100% with the current density increases. This relatively high-rate capability and almost constant coulombic efficiency once again confirm that the Li₂Co₂(MoO₄)₃ undergoes pseudocapacitance mechanism through redox reaction and ion intercalation in the bulk material as the BET surface area is relatively low (17.65 m² g⁻¹).^[12,30,31] However, to follow the influence of ion size on the electrochemical performances, galvanostatic charge-discharge test was also performed in NaOH and KOH electrolytes. In all electrolytes, the as-prepared material shows a pseudocapacitive behavior. It is interesting to notice that the capacity obtained in lithium-based electrolyte is higher than those realized in Na- and K-based electrolytes (Figure 3d), which is in good agreement with the CV results. This is obviously attributed to the small size of lithium ion, which is easier intercalated and also the presence of the Li in the crystal structure.

Figure 3e displays the cycling performance, which is another key factor to achieve the requirement for supercapacitor applications. The annealed $\rm Li_2Co_2(MoO_4)_3$ sample exhibits an outstanding capacity retention of 99% and 91% at 30 A g⁻¹ after 3000

and 10 000 charge-discharge cycles, respectively, much better than the uncalcined counterpart, which displays 62% capacity lost after 3000 cycles. Furthermore, to understand these outstanding properties, electrochemical impedance spectroscopy was performed in the frequency range from 0.01 Hz to 10 kHz at open circuit. From the Nyquist plots shown in Figure 3f, the annealed and uncalcined Li2Co2(MoO4)3 possess almost the same charge transfer resistance (R_{ct}) , which is represented by the diameter of the semicircle in the high-frequency region.^[32] The most remarkably difference comes from the slope in the Warburg region (low frequency), which is related to solid-state ion diffusion in the bulk material. Indeed, the annealed sample displays a high ion mobility and diffusion characterized by a steeper slope compared with the uncalcined counterpart, which explains the improved electrochemical performance of the calcined Li₂Co₂(MoO₄)₃ over the uncalcined counterpart.

For further evidence of ion intercalation in the bulk material, we performed an in situ XRD studies in LiOH and KOH electrolytes. The testing cell was constituted of the $\text{Li}_2\text{Co}_2(\text{MOO}_4)_3$ annealed at 350 °C and CFP operating as cathode and anode, respectively, at a scan rate of 1 mV s⁻¹ in the potential range of 0 to 1.6 V. The in situ XRD in LiOH electrolyte reveals an increase in the peak intensity at 21° (Figure S5, Supporting Information), which can be related to the lithium intercalation in the crystal structure. To the other side, the in situ XRD conducted in KOH displays a shift in the peak intensity at 45° is observed but more remarkably for Li-based electrolyte, which

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can be attributed to the presence of Li in the crystal structure. This small difference in the behavior of Li and K containing electrolyte is related to the crystal channel in the host material, which allows Li⁺ (small size \approx 0.73 Å) to intercalate without structure deformation while it is contrary for K⁺ (large size \approx 1.51 Å).

The above-obtained high electrochemical performances for $Li_2Co_2(MoO_4)_3$ annealed at 350 °C as electrode material for supercapacitor applications can be explained, in one hand, by the interconnected nanorods–nanoflakes morphology, which enhances the kinetics of ion transport at the electrode–electrolyte interface. In the other hand, these high performances are related to the crystallographic structure of the NASICON-type material possessing channels, which easily allow small-sized ions to intercalate and deintercalate without structural destruction.

Considering the practical application of the as-synthesized electrode material, an asymmetric supercapacitor (ASC) was further assembled using a reduced graphene oxide (RGO) film as a negative electrode and the Li₂Co₂(MoO₄)₃ operating as a positive one. The details of the synthesis and electrochemical characterization of RGO films are described in the Supporting Information.^[33] The optimal mass ratio between the positive and negative electrodes (m_+/m_-) is 0.36 in the ASC calculated based on the equation displayed in the Supporting Information.

The electrochemical performances of the assembled ASC were obtained by cyclic voltammetric and galvanostatic charge–discharge tests with a total mass of 2.47 and 7.4 mg for $\text{Li}_2\text{Co}_2(\text{MoO}_4)_3$ and RGO film, respectively. **Figure 4**a shows the CV curves obtained at various voltages in 2 M LiOH electrolyte at 10 mV s⁻¹. It is obviously seen that the curve surface area increases with the voltage increase. Also all the curves display an almost rectangular shape on which a couple of broad

anodic and cathodic peaks can be clearly observed indicating both contributions of double-layer capacitance from RGO film and faradaic pseudocapacitance from Li₂Co₂(MoO₄)₃. Furthermore, increasing the potential window at higher value of 1.8 V, more redox peaks occur at the cathode indicating the large contribution of pseudocapacitive charge transfer process. Figure 4b displays the specific capacitance of the asymmetric capacitance as a function of voltage at 10 A g⁻¹. The capacitance increases greatly from 65 to 130 F g^{-1} with the increase of the operating voltage range from 1.2 to 1.8 V, which leads to the improved electrochemical performances. From Figure 4c, the specific gravimetric capacitance calculated for the as-assembled ASC in the 1.8 V voltage window decreases from 160 to 116 F g^{-1} corresponding to a high-rate capability of 77% with the increase of current density from 1 to 20 A g⁻¹ and an average coulombic efficiency around 99%. Moreover, the device displays outstanding capacitance retention of 98% after being tested for 8000 cycles at 20 A g⁻¹ at 1.8 V voltage, which is comparable with some previously reported ASCs.^[34,35]

As it is well known that the large operating voltage is a critical factor to increase the devices energy density and average power density. Notably, as displayed in the Ragone plot (Figure 4d), our ASC delivers a maximum energy density of 71.63 W h kg⁻¹ at power density of 0.91 kW kg⁻¹ and remains 52.17 W h kg⁻¹ at 18.23 kW kg⁻¹, calculated according to the equation depicted in Supporting Information, which are considerably higher and in the same order as the recently reported values.^[36,37] Additionally, this energy and average power density are very competitive with Li-ion batteries and significantly higher than those of currently used electrochemical capacitors.

In summary, we have successfully synthesized interconnected nanorods–nanoflakes $Li_2Co_2(MoO_4)_3$ Nasicon-type structure by a reproducible mild hydrothermal method. The



Figure 4. a) CV curves of the $Li_2Co_2(MOO_4)_3//RGO$ asymmetric supercapacitor in different voltage windows at 10 mV s⁻¹. b) The gravimetric specific capacitance and coulombic efficiency of the $Li_2Co_2(MOO_4)_3//RGO$ ASC calculated based on the galvanostatic charge–discharge at 10 A g⁻¹ as a function of voltage window. c) The rate capability of $Li_2Co_2(MOO_4)_3//RGO$ device at 1.8 V voltage from 1 to 20 A g⁻¹. d) Cycling performance of $Li_2Co_2(MOO_4)_3//RGO$ device at 1.8 V voltage from 1 to 20 A g⁻¹. d) Cycling performance of $Li_2Co_2(MOO_4)_3//RGO$ asymmetric supercapacitor at a deded for comparison.

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as-prepared compound serves as electroactive material for supercapacitor and delivers a high rate capability of 67% (from 1055 to 700 F g^{-1}) for a current density range from 1 to 50 A g^{-1} with a higher capacity retention (91%) after tested for 10 000 cycles at 30 A g⁻¹. These high performances are related to the crystallographic structure of the NASICON material possessing channels that easily allow small-sized ions to intercalate and deintercalate without structure destruction and the interconnected nanorod-nanoflake morphology, which enhances the kinetics of ion transport at electrode-electrolyte interface. Furthermore, we have assembled an ASC with Li₂Co₂(MoO₄)₃ and RGO film working as cathode and anode, respectively. The device displays high energy density of 71.63 W h kg⁻¹ at power density of 0.91 kW kg⁻¹, which approaches that of Li-ion batteries, in the extended operating voltage of 1.8 V. It also retains 98% of its initial capacitance after 8000 cycles at a current density of 20 A g⁻¹. As the NASICON-type materials are large family of many compounds, this encouraging result opens up an opportunity to consider these materials for advancing the electrochemical performances of supercapacitors.

Experimental Section

Material Preparation: The interconnected nanorods-nanoflakes Li₂Co₂(MoO₄)₃ were uniformly synthesized on conductive substrate (3 D Ni foam, carbon cloth, and CFP) by mild condition hydrothermal method (Method, Supporting Information). For further crystallization, the obtained material was annealed at 350 °C for 1 h in the air with increase temperature rate of 5 °C min⁻¹. The mass loading of the Li₂Co₂(MoO₄)₃ was about 1.04 mg cm⁻² calculated based on the mass average of 10 samples.

Materials Characterization: The chemical composition and the morphology of the as-prepared material were determined by powder XRD (Burker D8 Advanced X-ray diffractometer), TG, and DTA on a STA449c/3/G (NETZSCH), BET surface area with Tristar II 3020 instrument, field-emission SEM (JEOL7100F), and high-resolution TEM (JEM-2100F STEM/EDS), respectively. The electrochemical properties were carried out in a typical three-electrode cell using Autolab Potentiostat Galvanostat (Autolab PGSTAT 302N). The tests were conducted in alkaline electrolyte with as-synthesized materials on the 3D nickel foam as working electrode, Ag/KCI SCE, and Pt foil as reference and counter electrode, miss were performed in different alkaline electrolytes and the full cell was assembled with our synthesized material as cathode and RGO as anode.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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