Sol–Gel Synthesis of Mesoporous \( \alpha \text{-Co(OH)}_2 \) and Its Electrochemical Performance Evaluation

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ABSTRACT: Mesoporous structures of \( \alpha \text{-Co(OH)}_2 \) have been selectively synthesized by a simple one-pot sol–gel process using propylene oxide as gelation agent. Synthesized material is investigated for its crystal structure (crystallinity, phase), morphology (shape, size, surface area, porosity), and electrochemical performance. The specific capacity of the as-synthesized \( \alpha \text{-Co(OH)}_2 \) is 430 C/g, when the electrodes underwent charge/discharge cycling in 6 M potassium hydroxide at 1 A/g specific current. Enthrallingly, capacity retentions of up to 86 and 80% were found over 2000 and 3000 cycles, respectively, at a relatively high specific current of 10 A/g. The as-synthesized material is studied as full cells or complete devices, wherein it delivered capacities of about 80 and 25 C/g in symmetric and asymmetric modes, respectively, at a current of 1 A/g. High capacity is ascribed to the uniform porous nature of the material with considerable surface area. With an extraordinary cycle life and charge-storage capacity, the material prepared is an able contender for supercapacitor electrodes.

INTRODUCTION

Shortage of crude oil and global warming have led to increased focus on alternate energy-storage devices and conversion systems, especially supercapacitors and batteries. There is an immediate need for a breakthrough in this particular area of research so as to counter the next-generation meager carbon and unceasing economy. Primarily, rechargeable batteries are used in electric vehicles as power devices and energy-storage devices, in the case of solar and wind energy harvesting. Power density is the key issue related to these secondary batteries, which arises due to the slow kinetics of cationic insertion/deinsertion within the crystalline framework of electrode materials. Unlike batteries, the fundamental mechanism which drives the high power density of supercapacitors is the dependence of charge storage on the electrode surface reactions, either in electrochemical double-layer supercapacitor or pseudocapacitive materials. The limitation of the extent of possible reactions at or near the electrode surface tends supercapacitors to possess lower energy density, which is a key point to note. This tends us to put enormous effort in search of suitable materials with higher energy density.

Cobalt hydroxide is a promising material owing to its widespread industrial applications as solar absorber, catalyst for oxygen evolution reaction and oxygen reduction reactions, gas sensors, photovoltaic cells, batteries, supercapacitors, etc. The hydroxides of cobalt are familiar in crystallized \( \alpha \) - and \( \beta \)-polymorphic forms. The \( \alpha \text{-Co(OH)}_2 \) (hydratolcite-like) is composed of stalked monolayers of Co(OH)$_2$\( \delta \) with anions like NO$_3^-$, CO$_3^{2-}$, and Cl$^-$ intercalated. \( \beta \text{-Co(OH)}_2 \) is isostructural with brucite-like molecular structures consisting of octahedral layers of ionic cobalt with –OH ion coordinated. Expanded interlayer spacing in \( \alpha \) form compared to that in \( \beta \) polymorph results in higher electrochemical activity. There are many successful synthetic routes, namely, hydrothermal/solvothermal, precipitation, electrodeposition, and sol–gel methods. Among these, the sol–gel method provides some advantages mainly concerning the capacity to give a solid-state compound from a chemically homogeneous starting material. Many complex inorganic materials like ternary/quaternary oxides can be synthesized at lower processing temperatures and shorter synthesis times by controlling the entropy of the solution state and by effective atomic-level blending of reactants. Also, the sol–gel chemistry enables control over material morphology and size.

It is always necessary to understand and designate the nature of the electrochemical behavior of the material under study. In carbon materials, a rectangular cyclic voltammogram is obtained, which is its electrochemical signature due to electrochemical double-layer capacitor (EDLC) arising from the potential dependency of the surface density of electrostatically stored charges at the electrode interfaces. Materials like MnO$_2$/RuO$_2$ exhibit a similar nature, which derives from reactions that are faradaic in nature, involving charge passage across the double layer. This pseudocapacitance originates from quick and reversible redox reactions involving interconversions of redox states in the electrode material and the corresponding cationic insertion from electrolyte. However, in faradaic or battery-type materials, there exists dependency between charge stored and potential range, which is nonlinear, and cobalt hydroxide is one such material.

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In this report, α-Co(OH)$_2$ synthesized from sol–gel route using propylene oxide as a gelation agent is studied for its electrochemical behavior as a supercapacitor electrode material. It delivers capacities of 430 C/g at 1 A/g and 110 C/g at a considerably high specific current of 20 A/g in 6 M KOH. Interestingly, it retains 80% of initial capacity over 3000 cycles at 10 A/g, attesting its reliability as supercapacitor electrode material. Furthermore, it exhibits a high capacity of 80 C/g at 1 A/g in symmetric mode and a capacity of 25 C/g in asymmetric mode.

RESULTS AND DISCUSSION

In this report, α-Co(OH)$_2$ synthesized from sol–gel route using propylene oxide as a gelation agent is studied for its electrochemical behavior as a supercapacitor electrode material. It delivers capacities of 430 C/g at 1 A/g and 110 C/g at a considerably high specific current of 20 A/g in 6 M KOH. Interestingly, it retains 80% of initial capacity over 3000 cycles at 10 A/g, attesting its reliability as supercapacitor electrode material. Furthermore, it exhibits a high capacity of 80 C/g at 1 A/g in symmetric mode and a capacity of 25 C/g in asymmetric mode.
acids, alkalinity of epoxide will be also low. It is the reason for the condition wherein reaction between epoxide and the complex will not result in the evolution of $\beta$-Co(OH)$_2$ in the absence of NH$_3$F. However, pure $\alpha$ phase can be obtained if F$^-$ concentration is regulated.$^{13}$

Figure 1a presents the X-ray diffraction (XRD) data of as-synthesized Co(OH)$_2$ powder. The diffraction signals are catalogued as $\alpha$-Co(OH)$_2$ (JCPDS file no. 74-1057). The prominent peaks at 2$\theta$ values of 11.2, 23, 33, 34, 38.5, 45.5, 59, and 60.5$^\circ$ are related to the planes (003), (006), (101), (012), (015), (018), (110), and (113) respectively.$^{13,18}$ No impurities are present in the compound.

Figure 1b–e depicts the TEM images in different magnifications of the synthesized compound $\alpha$-Co(OH)$_2$, including higher-resolution image (HRTEM) and selected area electron diffraction (SAED) pattern. The images (b) and (c) suggest amorphous and porous structures possessing mass of tunnels in between the particles. The loosely packed porous network leads to voids/tunnels from disorganized dispersal of $\alpha$-Co(OH)$_2$ particles. The HRTEM image of the sample in Figure 1d presents unambiguous lattice fringes with a lattice fraction (SAED) pattern. The images (b) and (c) depict the TEM images in different magnifications of the synthesized compound $\alpha$-Co(OH)$_2$.

To examine the surface area and porosity of the synthesized compound, N$_2$ adsorption–desorption isotherms were registered (Figure 2a). The specific surface area was determined from the Brunauer–Emmett–Teller (BET) approach from adsorption curves of isotherms in the $p/p_0$ range of 0.1–0.2. Adsortion and desorption profiles show a loop at higher relative pressure, reflecting porous essence of the compound. It is seen that 70 cm$^3$/g of N$_2$ is adsorbed at $p/p_0 = 0.99$, possessing a specific surface area of 14.1 m$^2$/g. The Barrett–Joyner–Halenda (BJH) curves depict (Figure 2b) pore size distribution prominently at around 4 nm and narrow distribution at 40 nm. Thus, the BET study infers the mesoporous character of the synthesized $\alpha$-Co(OH)$_2$.

Electrochemical investigations of $\alpha$-Co(OH)$_2$ electrodes were performed by cyclic voltammetry (CV), galvanostatic charge/discharge cycling, and impedance spectroscopy in 6 M KOH electrolyte. Figure 3 depicts the results of a three-electrode system. Figure 3a shows CVs of cobalt hydroxide electrodes in the voltage range of $-0.7$–$0.7$ V at varied scan rates ($5$–$100$ mV/s). Strong peaks of currents related to faradaic redox reaction can be observed in the voltammograms, which prove the faradaic type of the transition-metal oxide/metal hydroxide-related compounds. This clearly differs from EDLC, which generally gives a rectangular shape. Higher peak current values with incremental scan rates prove the influence of scan rate on currents, suggesting tremendous rate performances. Co being a transition metal shows variable stable oxidation states ($Co^{2+}/Co^{3+}$ and $Co^{3+}/Co^{4+}$), thereby contributing to faradaic capacitance.$^{10,13,16,19–22}$ The possible mechanism can be represented as follows. Furthermore, voltammograms exhibit exceptional reversibility of the concerned electrode processes.

\[
\text{Co(OH)}_2 + \text{OH}^- \rightarrow \text{CoOOH} + \text{H}_2\text{O} + \text{e}^- \quad (1)
\]

\[
\text{CoOOH} + \text{OH}^- \rightarrow \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^- \quad (2)
\]

\[
\text{Co}_3\text{O}_4 + 4\text{OH}^- \rightarrow 3\text{CoO}_2 + 2\text{H}_2\text{O} + \text{e}^- \quad (3)
\]

Charge/discharge profiles at different specific currents are given in Figure 3b. The characteristics of these loops of same kind of discharge plateaus are in accordance with their corresponding CVs and can be attributed to the faradaic processes taking place in charge/discharge cycling. The capacity values based on charge/discharge experiments are shown in Figure 3c. The figure exhibits a superior SC of 430 C/g at a specific current of 1 A/g and an SC of 110 C/g at an appreciably high specific current of 20 C/g. As electrochemical stability, cyclability, and Coulombic efficiency are the primary necessities of supercapacitor electrode materials for practical applications, the materials were tested for long charge/discharge cycles at high current. Figure 3d describes the electrode stability and Coulombic efficiency of $\alpha$-Co(OH)$_2$ registered at 10 A/g for 3000 continuous cycles. Up to initial 500 cycles, the capacity was found to fade and thereafter it gets stabilized up to around 3000 cycles. A remarkable performance of the compound is that it shows 86% capacity retention up to 2000 cycles and 80% up to 3000 cycles. Coulombic efficiency was found to be around 86% at the beginning, which got improved, reaching a maximum of 98% at the 2500th cycle without larger fluctuations up to 3000 cycles. Electrochemical impedance spectroscopy (EIS) experiment was done to
elucidate the electrochemical nature of the materials. Figure 3e shows the Nyquist plot. It can be observed that the curve is composed of a discrete high-frequency semicircle and a spike in the region of low frequency. Ohmic resistance of the electrolyte and intrinsic resistance of the electrode material contribute to solution resistance $R_s$, which is located at the crossing with the $Z'$ axis, possessing a value of 0.5 Ω. Charge-transfer resistance $R_{ct}$ for the electrode is found to be nearly 1 Ω. In the low-frequency region, the straight line immediately after the semicircle is the Warburg resistance reflecting the diffusion process’s kinetics of electrolyte ions on the electrodes. The slope of the tail is clearly lower than the standard Warburg slope of 1, referring to the faradaic nature of the reaction mechanism responsible for charge storage.\textsuperscript{23,24}

There are quite a few research findings on the supercapacitive performance of cobalt hydroxides prepared from various routes, excluding sol–gel processing. Chou et al. fabricated cobalt hydroxide films on steel mesh and examined their supercapacitor application in 1 M KOH. They exhibit 220 C/g at 0.1 mA/g and 81% capacity retention over 3000 cycles.\textsuperscript{10} Wang et al. synthesized cobalt hydroxide by following the precipitation route. They claimed 429 C/g at 1 A/g in 2 M KOH.\textsuperscript{25} Mondal et al. used surfactant-free chemical route to synthesize $\beta$-Co(OH)$_2$ which exhibits 249.6 C/g at 1 A/g in 1 M KOH.\textsuperscript{26} Carbon fiber loaded with $\alpha$-Co(OH)$_2$ was studied.
for its supercapacitive behavior in 1 M LiOH, and it showed 193.3 C/g at 1 mA/cm² with 92% capacity retention over 2000 cycles.27 Du et al. published the synthesis of microsphere of β-phase of cobalt hydroxide showing an SC of 108.5 C/g at 2 A/g in 6 M KOH. Their hybrids with graphene show 216.5 C/g.28 In the recent past, Huang et al. have prepared flowerlike porous cobalt hydroxide and its composites of graphene to study their supercapacitive behavior in 6 M KOH. As-synthesized Co(OH)₂ (surface area, 39.1 m²/g) showed an SC of 60 C/g and its graphene composite (surface area, 97.9 m²/g) showed 192 C/g at 1 A/g.29 Thus, capacity values of 430 and 110 C/g at 1 and 20 A/g, respectively, are an
extraordinary achievement of α-phase of cobalt hydroxide synthesized by simple sol–gel route. A significant value of capacity at reasonably high specific area attests its high power capability. The superior electrochemical performance of the material is ascribed to the known faradaic 1–3 involving the interaction of metal hydroxide and KOH. Mesoporous characteristic with appreciable surface area associated with significant pore volume significantly adds to superior capacity by facilitating effortless riddling of ions of the electrolyte, which essentially shortens the diffusion.

Figure 4a,c shows the cyclic voltammograms of α-Co(OH)₂ symmetric and asymmetric capacitors. The voltammograms show appreciable reversibility in both the cases. However, in the case of symmetric capacitor, CV shows comparatively larger integrated area, indicating higher electrochemically active and thereby high capacity. The charge/discharge profiles for both symmetric and asymmetric capacitors are presented in Figure 4b,d, and the corresponding capacity values are shown in Figure 4e. Symmetric capacitor delivers an SC of 80 C/g at 1 A/g compared to that of asymmetric mode with 25 C/g. Achievement of the device in symmetric mode at 10 A/g is attractive, showing an SC of 65 C/g. We further examined the energy and power densities of the systems, and the results are presented in Figure 4e. Symmetric device performs better than the asymmetric one. The symmetric device was able to deliver a high energy density of 40 W/kg at the power density of 0.6 W/kg and still kept a remarkable energy density of 32.5 W/kg as the power density was increased to 8.1 W/kg. Superiority of the device can be credited to Co(OH)₂, which is a faradaic one, which contributes from both the electrodes of symmetric capacitor.

### CONCLUSIONS

We successfully designed α-Co(OH)₂ mesoporous structures selectively through a simple sol–gel procedure. The designed material exhibited a characteristic architecture of loosely packed porous network. The as-synthesized compound exhibits an appreciably great specific capacity of 430 C/g at 1 A/g and shows 86% retention of capacity over 2000 charge/discharge sweeps and about 80% up to 3000 cycles. Symmetric capacitor showed 80 C/g, and asymmetric capacitor showed 25 F/g at 1 A/g, which is quite interesting. This simple procedure of synthesis results in the formation of α-polymorph of cobalt hydroxide having unvaried porosity and remarkable surface area, which could facilitate small charge and ion diffusion lengths and very high transport rates. Therefore, propylene oxide-mediated sol–gel synthesis is a versatile route to selectively aim at α-Co(OH)₂ for supercapacitor electrodes with better specific capacities and notable cycling stability.

### EXPERIMENTAL SECTION

**Synthesis of α-Co(OH)₂.** CoCl₂·6H₂O (2.86 g) and NH₄F (0.11 g) were dissolved in 20 mL of double-distilled water to obtain a clear solution. Precipitation agent propylene oxide (9.4 mL) was mixed with the above mixture under stirring and a pink precipitate was formed after 30 min, which changes to green after a couple of hours under continuous stirring. The resulting precipitate was kept under stirring for 12 h. The resulting compound was rinsed many times with distilled water. The precipitate was dried in air at ambient condition.

**Characterization Methods.** Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical diffractometer with Cu Kα source (wavelength, 1.5438 Å). Surface area and pore size distribution were calculated by Micromeritics surface area analyzer model ASAP 2020. X-ray photoelectron spectra were recorded on an AXIS ULTRA X-ray photoelectron spectrometer. Microscopic analyses were done using an FEI Tecnai T-20 200 kV transmission electron microscope equipped with an EDAX facility.

**Preparation of Electrodes and Electrochemical Characterization.** For fabrication of electrodes, 70 wt % α-Co(OH)₂, 15 wt % conductive carbon (Ketjen black), and 15 wt % poly(vinylidene fluoride) were added to the mixture to form a semisolid, which was brush-coated on a carbon paper with an overall 1 cm² geometrical area and vacuum-dried at 100 °C. Coating and drying exercises were duplicated to obtain the mass of active material in the range of 0.8–1 mg/cm² and finally dried for 12 h. A three-electrode glass cell was designed using α-Co(OH)₂-coated carbon paper, platinum, and saturated calomel electrode (SCE) as the working, counter, and reference electrodes, respectively.

All potential values are reported with reference to SCE. Cyclic voltammetry (CV) and galvanostatic charge/discharge experiments were performed using Bio-Logic SA multichannel potentiostat/galvanostat model VMP3. Electrochemical impedance spectroscopy (EIS) measurements (frequency window, 0.01 Hz to 100 kHz) with an alternating voltage perturbation of 5 mV were made using Electrochemical Analyzer model CH1608C. Galvanostatic charge/discharge cycling tests between −0.4 and 0.5 V were done, and the discharge specific capacity (C) was calculated using the relation $C = It/m$, where $I$ is the current, $t$ is the discharge time, and $m$ is the mass of the active material loaded on the electrode. In the case of two-electrode system or experiments with full cell, the compound was coated on two carbon papers of 1 cm² area and absorptive glass mat (soaked previously in the electrolyte) was used as separator. The whole system was sealed and evaluated for its electrochemical performance. In the case of full cell in asymmetric mode, one of the electrodes was activated YZC (Yanzhou Coal Mining Co. Ltd.) China carbon.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

1. Conway, B. E. Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications; Kluwer Academic/Plenum Publishers: New York, 1999; pp 1–39.
2. Arićà, A. S.; Bruce, P. G.; Scrosati, B.; Tarascon, J. M.; Schalkwijk, W. V. Nanostructured materials for advanced energy conversion and storage devices. Nat. Mater. 2005, 4, 366–377.
3. Simon, P.; Gogotsi, Y. Materials for electrochemical capacitors. Nat. Mater. 2008, 7, 845–854.
(4) Hall, P. J.; Mirzaein, M.; Fletcher, S. I.; Sillars, F. B.; Rennie, A. J. R.; Shitta, G. O. B.; Wilson, G.; Cruden, A.; Carter, R. Energy storage in electrochemical capacitors: designing functional materials to improve performance. Energy. Environ. Sci. 2010, 3, 1238–1251.

(5) Wang, G.; Zhang, L.; Zhang, J. A review of electrode materials for electrochemical supercapacitors. Chem. Soc. Rev. 2012, 41, 797–828.

(6) Hou, J.; Shao, Y.; Ellis, M. W.; Moore, R. B.; Yi, B. Graphene-based electrochemical energy conversion and fuel cells, supercapacitors and lithium ion batteries. Phys. Chem. Chem. Phys. 2011, 13, 15384–15402.

(7) Patil, S.; Raut, S.; Gore, R.; Sankapal, B. One-dimensional cadmium hydroxide nanowires towards electrochemical supercapacitor. New J. Chem. 2015, 39, 9124–9131.

(8) Ma, X.; Zhang, W.; Kong, L.; Luo, Y.; Kang, L. NiMoO₄-modified MnO₂ hybrid nanostructures on nickel foam: electrochemical performance and supercapacitor applications. New J. Chem. 2015, 39, 6207–6215.

(9) Hu, C. C.; Chang, K. H.; Lin, M. C.; Wu, Y. T. Design and Tailoring of the Nanotubular Arrayed Architecture of Hydrous RuO₂ for Next Generation Supercapacitors. Nano Lett. 2006, 6, 2690–2695.

(10) Chou, S.-L.; Wang, J.; Liu, H.; Dou, S. Electrochemical Deposition of Porous Co(OH)₂ Nanoflake Films on Stainless Steel Mesh for Flexible Supercapacitors. J. Electrochem. Soc. 2008, 12, A926–A929.

(11) Xu, H.; Zhang, C.; Zhou, W.; Li, G. Co(OH)₂/RGO/NiO sandwich-structured nanotube arrays with special surface and synergistic effects as high-performance positive electrodes for asymmetric supercapacitors. Nanoscale 2015, 7, 16932–16942.

(12) Xie, H.; Tang, S.; Gong, Z.; Vongehr, S.; Fang, F.; Li, M.; Meng, X. 3D nitrogen-doped graphene/Co(OH)₂-nanoplate composites for high-performance electrochemical pseudocapacitors. RSC Adv. 2014, 4, 61753–61758.

(13) Cui, H.; Ma, W.; Wang, L.; Xue, J. Preparation of a-Co(OH)₂ monolayer nanosheets by an intercalation agent-free exfoliation process. J. Sol-Gel Sci. Technol. 2016, 78, 293–298.

(14) Brenzer, G.; Maier, W. F. AMORPHOUS POROUSMIXED OXIDES: Sol-Gel Ways to a Highly Versatile Class of Materials and Catalysts. Annu. Rev. Mater. Res. 2006, 36, 281–331.

(15) Ranganatha, S.; Kumar, S.; Penki, T. R.; Kishore, B.; Munichandraiah, N. Co₂(OH)₃Cl xerogels with 3D interconnected mesoporous structures as a novel high-performance supercapacitor material. J. Solid State Electrochem. 2017, 21, 133–143.

(16) Ranganatha, S.; Munichandraiah, N. Synthesis and performance evaluation of novel cobalt hydroxide chlorides for electrochemical supercapacitors. J. Solid State Electrochem. 2017, 21, 939–946.

(17) Brousse, T.; Belanger, D.; Long, J. W. To Be or Not To Be Pseudocapacitive? J. Electrochem. Soc. 2015, 162, A5185–A5189.

(18) Gao, Z.; Yang, W.; Yan, Y.; Wang, J.; Ma, J.; Zhang, X.; Xing, B.; Liu, L. Synthesis and Exfoliation of Layered α-Co(OH)₂ Nanosheets and Their Electrochemical Performance for Supercapacitors. Eur. J. Inorg. Chem. 2013, 4832–4838.

(19) Liu, Y.; Jiang, G.; Sun, S.; Xu, B.; Zhou, J.; Zhang, Y.; Yao, J. Decoration of carbon nanofibers with NiCo₂S₄ nanoparticles for flexible asymmetric supercapacitors. J. Alloys Compd. 2018, 731, 560–568.

(20) Sun, S.; Jiang, G.; Liu, Y.; Zhang, Y.; Zhou, J.; Xu, B. Growth of MnO₂ nanoparticles on hybrid carbon nanofibers for flexible symmetrical supercapacitors. Mater. Lett. 2017, 197, 35–37.

(21) Chen, H.; Jiang, G.; Yu, W.; Liu, D.; Liu, Y.; Li, L.; Huang, Q.; Tong, Z. Electrospun carbon nanofibers coated with urchin-like ZnCo₂O₄ nanosheets as a flexible electrode material. J. Mater. Chem. A 2016, 4, 5958–5964.

(22) Liu, Y.; Jiang, G.; Sun, S.; Xu, B.; Zhou, J.; Zhang, Y.; Yao, J. Growth of NiCo₂S₄ nanotubes on carbon nanofibers for high performance flexible Supercapacitors. J. Electroanal. Chem. 2017, 804, 212–219.

(23) Shivakumara, S.; Penki, T. R.; Munichandraiah, N. High specific surfacearea α-Fe₂O₃ nanostructures as highperformance electrodematerial for supercapacitors. Mater. Lett. 2014, 131, 100–103.