Bricklike $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ as an Active/Inactive Composite for Lithium-Ion Batteries with Enhanced Rate Performances

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ABSTRACT: Transition-metal oxides are considered as promising anode materials because of the high theoretical specific capacities. However, the fast capacity fading and unstable cycling performance restricted their electrochemical performance. To achieve fast and stable lithium storage capability, in this work, bricklike $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ is synthesized via a modified Pechini method with the assistance of the $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ surfactant. The as-obtained $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ ternary oxides exhibit stable structural stability, which may be attributed to the in situ formed CaO layers during the first discharge process. When tested as an anode material in lithium-ion batteries (LIBs), bricklike $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ exhibits an excellent reversible capacity of 517 mA h g$^{-1}$ at 1 C after 200 cycles. Even at the high rate of 3 C, the discharge capacity can still reach 392 mA h g$^{-1}$ after 200 cycles. It reveals a great application prospect in anode materials of LIBs.

1. INTRODUCTION

The growing demand of consumer electronics and electric vehicles (EVs) has sparked a strong interest in developing high-performance electrode materials of lithium-ion batteries (LIBs). The limited theoretical capacity of commercial graphite (300–350 mA h g$^{-1}$) stimulates the development of the next-generation anode materials. Among them, the specific capacity of the transition-metal cobalt oxides (CoO, Co$_3$O$_4$) can reach up to 700–1000 mA h g$^{-1}$, which is considered as the promising anode material of LIBs. Nevertheless, the application of the cobalt oxides is limited by the poor capacity retention and sluggish rate performance, which commonly result from the aggregation of metallic nanoparticles and the huge volume variation during cycling.

By partially replacing Co ions with cheap and environmentally friendly metal ions, the construction of layered Co–Ca-based ternary oxides, such as $\text{Ca}_2\text{Co}_2\text{O}_5$, $\text{Ca}_3\text{Co}_4\text{O}_9$, and $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$, has been taken into account for improving the electrochemical performance of traditional cobalt oxides. For $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$, CoO layers and rock salt CaO layers are arranged alternately in the $c$-axis direction. Co–Ca-based oxides transform into metal nanodomains (Co) embedded in the Li$_2$O and CaO matrix during the cycling processes, while the inactive CaO is performed as the structural buffer layer.

Typically, Co–Ca-based ternary oxides are synthesized via a solid-state route by heating calcium and cobalt sources at high temperature for several hours. Despite its simplicity and operability, the products are frequently prepared with large particle size and inferior degree of chemical homogeneity, thus leading to the limited electrochemical performance. For instance, the compound $\text{Ca}_2\text{Co}_2\text{O}_5$ prepared by the high-temperature solid-state reaction was reported to exhibit a reversible capacity of 365–380 mA h g$^{-1}$, which is just comparable to that of graphite. On the contrary, the wet-chemical process offers the uniform mixing conditions and mild reaction environment, which can guarantee the crystallinity, purity, and uniform particle size of the final products. Citrate sol–gel method is one of the most typical routes for the preparation of Co–Ca-based ternary oxides. This reaction promotes the intimate mixing of reactants on the atomic scale and lowers the reaction temperature. For instance, nanosized $\text{Ca}_3\text{Co}_4\text{O}_9$ particles could be prepared via PEG 400-assisted or starch-assisted sol–gel methods. When used as an anode material for LIBs, nanosized...
Ca$_3$Co$_4$O$_9$ exhibited enhanced cycling stability compared with nanosized Co$_3$O$_4$ and commercial Co$_3$O$_4$. It delivers a stable reversible capacity of $\sim 500$ mA h g$^{-1}$ after 50 cycles. Recently, some other synthetic methods have also been reported for the preparation of performance-optimized Ca$_3$Co$_4$O$_9$ compounds, for instance, Ca$_3$Co$_4$O$_9$ nanofibers obtained by solution blow spinning, polycrystalline Ca$_3$Co$_4$O$_9$ materials synthesized by sintering and spark plasma sintering, and Cr-doped Ca$_3$Co$_4$O$_9$ materials synthesized by the thermal hydrodecomposition method. However, as for another layered Co–Ca-based ternary oxides of Ca$_9$Co$_{12}$O$_{28}$, the currently reported synthetic methods can hardly meet the demands for the sake of improving their structural stability and rate capability. Wu’s group reported the universal synthesis method of porous Ca$_9$Co$_{12}$O$_{28}$ nanowires via microemulsion reaction and thermal decomposition. When operating under the current rates of 0.1, 1, 2, 3, 4, and 0.1 C, the discharge capacities reached 241, 115, 72, 55, 46, and 208 mA h g$^{-1}$, respectively. Despite the good Coulombic efficiency, the specific capacity and rate capability are far from meeting the needs of practical applications. In our previous work, we fabricated Ca$_9$Co$_{12}$O$_{28}$ nanoparticles with a size of about 25 nm through a Pechini method. The initial charge/discharge capacity reached 908/816 mA h g$^{-1}$, together with the stabilized capacity of 210 mA h g$^{-1}$ after 50 cycles, which was significantly improved compared with other reported works. However, further work still needs to be conducted for the enhancement of cycling stability and discharge capacity.

In this article, bricklike Ca$_9$Co$_{12}$O$_{28}$ is synthesized via a modified Pechini method with the participation of the C$_{12}$H$_{25}$SO$_4$Na (SDS) surfactant, which offers the delicate combination of different advantages. First, the SDS surfactant can decrease the interfacial energy between intermediate particles and the solvent, thus achieving the control of crystal growth and particle sizes. Therefore, in the as-obtained products, the homogeneity and crystallinity are ensured. Second, the reaction kinetics is improved in bricklike Ca$_9$Co$_{12}$O$_{28}$ because of the abundant ionic diffusion channels, thus leading to the enhanced rate performance. Furthermore, because of the layered distribution of metal ions in the chains of polymeric gels, the primary particles can be protected from agglomeration. To the best of our knowledge, it is the first time that bricklike Ca$_9$Co$_{12}$O$_{28}$ is prepared with the assistance of the SDS surfactant via a modified Pechini route. This work may provide a novel and facile strategy for the fabrication of Ca$_9$Co$_{12}$O$_{28}$ anode materials.

Figure 1. (a) XRD pattern of bricklike Ca$_9$Co$_{12}$O$_{28}$. (b) SEM image of bricklike Ca$_9$Co$_{12}$O$_{28}$. (c,d) TEM images of bricklike Ca$_9$Co$_{12}$O$_{28}$ at low and high magnification. (e) EDX spectra of bricklike Ca$_9$Co$_{12}$O$_{28}$.
2. EXPERIMENTAL SECTION

2.1. Synthesis of Bricklike Ca$_9$Co$_{12}$O$_{28}$. All the chemical reagents here were of analytical grade and used without further purification. In a typical synthesis, 0.015 mol of Ca(NO$_3$)$_2$·4H$_2$O and 0.02 mol of Co(NO$_3$)$_2$·6H$_2$O were dissolved in 30 mL of deionized water, followed by the addition of 0.07 g/L SDS. After stirring for 1 h at 40 °C, 0.07 mol of citric acid was added slowly and stirred for 2 h to form chelates between citric acid and metal ions. After adding 0.28 mol of ethylene glycol to the stirring solution under 80 °C, the polymeric resin was preliminarily formed. Then, the above solution was distilled to exclude water added at the first stage. To completely form the polymeric resin, the obtained solution was heated in a draught cupboard at 150 °C. The Ca$_9$Co$_{12}$O$_{28}$ materials were finally obtained after the calcination of polymeric resin in air at 850 °C for 4 h.

2.2. Characterization. The phase of the final products was characterized by powder X-ray diffraction (XRD; Bruker, Germany) with a Cu Kα radiation source (λ = 0.15418 nm). The microstructure and morphology of the samples were observed by transmission electron microscopy (TEM; FEI TECNAI20, USA) and field-emission scanning electron microscopy (ZEISS, Germany) coupled to the energy-dispersive X-ray spectroscopy (EDX) analysis related to the chemical composition.

2.3. Electrochemical Measurement. The electrode active materials were composed of a Ca$_9$Co$_{12}$O$_{28}$ anode, conductive agents (acetylene black, Super P), and polymer binder polyvinylidene fluoride, with the weight ratio of 7:2:1. The mixture was uniformly ground for 30 min, and then the organic solvent of N-methyl pyrrolidone solution was added dropwise. The as-obtained slurry was cast onto Cu foil and dried at 100 °C for 12 h in a vacuum oven before being assembled in an argon-filled glovebox (MB-LABstar 1200/780, Germany). The coin-type cells (size: 2016) consisted of the working electrode, metallic lithium anode, separator (Celgard 2400), and nickel foam. LiPF$_6$ (1 M) in a mixture of ethylene carbonate, dimethylcarbonate, and diethyl carbonate (1:1:1, v/v) was used as the electrolyte. The galvanostatic charge and discharge tests were conducted on a Land battery test system (Wuhan, China) within the voltage range of 0.001−3 V versus Li$^+$/Li at a series of current densities at room temperature.

3. RESULTS AND DISCUSSION

The crystallographic structure of the as-obtained product has been identified by XRD as shown in Figure 1a. The sharp and high-intensity peaks are observed in bricklike Ca$_9$Co$_{12}$O$_{28}$, which can be assigned to the well-crystallized orthorhombic phase (JCPDS card no. 21-0139). It is worth noting that the (010) reflection shows high intensity, indicating that the crystallites are abundant in (010) facets along the ac plane. Figure 1b−d shows the morphological characterization of Ca$_9$Co$_{12}$O$_{28}$ materials. As observed from scanning electron microscopy (SEM) images (Figure 1b), bricklike structures are prepared in a two-dimensional (2D) structure with homogeneous distribution. Some of the bricklike structures expose their lateral planes, and the thickness reaches approximately 200 nm. Furthermore, their evident corners and edges can also be investigated. TEM images (Figure 1c,d) exhibit the frontal surface characters of bricklike Ca$_9$Co$_{12}$O$_{28}$. It can be seen that the bricklike structures are mainly stacked by 2D layered materials along specific direction. The uniform distribution of Ca$_9$Co$_{12}$O$_{28}$ samples should be mainly attributed to the mild reaction environment offered by the SDS surfactant. As observed in the EDX spectrum (Figure 1e), the uniform distribution of Ni, Mn, and O elements is investigated, together with the existence of the C element, which is mainly obtained from the thermal decomposition of polymer chains. The protective carbon layers on the compound surface can enhance the ionic/electronic conductivity and structural durability, thus yielding better electrochemical performance.

Depending on the experimental results, we propose the possible formation mechanism of bricklike Ca$_9$Co$_{12}$O$_{28}$ in Figure 2. Generally, the crystal growth involves nucleation and the subsequent growth of nuclei, during which the chelating ligands play a vital role in controlling the crystal shape.31−33 In
the initial stage, under the action of three carboxyl groups and one hydroxyl group of citric acid, the metal ions and citric acid form chelates through various reaction patterns. As the reaction proceeds, massive metal ions come together in a certain arrangement to form primary bricklike structures, which are three-dimensionally connected with each other via hydrogen bonds. The interaction between positively charged metal ions and the negatively charged SDS surfactant leads to selective adsorption of surfactant molecules on the bricklike structures. On the one hand, the uniform adsorption of the surfactant on bricklike structures enables their synchronous growth. On the other hand, after the addition of ethylene glycol, polymerization leads to the formation of an interrelated conductive network. Consequently, the stoichiometric metal ions can be confined in the polymer gels, which prevent the agglomeration of the primary nanoparticles. After the energy-efficient calcination, the Ca$_9$Co$_{12}$O$_{28}$ products can be obtained.

The redox process of bricklike Ca$_9$Co$_{12}$O$_{28}$ is evaluated by cyclic voltammetry (CV) in the voltage range of 0.005–3.0 V, and the corresponding data are presented in Figure 3. Noticeably, distinct changes can be observed in CV curves before and after activation, shown in Figure 3a, which may be attributed to the two different reaction processes. The oxidation peaks are shifted from 1.967 to 2.054 V, whereas the reduction curves are varied from 0.746 to 0.565 V. In addition, under the fast scan rate of 1 mV s$^{-1}$, the curves almost follow the same trajectory after activation, where little changes are observed in the consecutive CV curves (as shown in Figure 3b). This illustrates for the complete and stable intercalation/deintercalation process of lithium ions in the layered Ca$_9$Co$_{12}$O$_{28}$ materials. We further notice that the CV curves of bricklike Ca$_9$Co$_{12}$O$_{28}$ are almost identical to those of CoO anodes. This proves that the stable CaO layers do not take part in the electrochemical reaction after activation because of the high bond strength of CaO. From the characteristic peaks of the redox process, the reduction peaks at around 0.57 V are attributed to the reaction between lithium and the Ca$_9$Co$_{12}$O$_{28}$ anode, which lead to the formation of a CaO matrix, metallic Co nanoparticles, and Li$_2$O. In the oxidation process, two distinct peaks are observed at 1.12 and 2.05 V because of the formation of a CoO matrix, metallic Co nanoparticles, and Li$_2$O. The multistep reactions on the positive-electrode side of the Ca$_9$Co$_{12}$O$_{28}$/Li half-cells can be written as follows:

\[
\text{Ca}_9\text{Co}_{12}\text{O}_{28} + 38\text{Li} \rightarrow 9\text{CaO} + 12\text{Co} + 19\text{Li}_2\text{O} \quad (1\text{st discharge})
\]
The cyclic property of bricklike Ca$_9$Co$_{12}$O$_{28}$ is also evaluated. In addition to that, the according to the as-mentioned equation and the formation of this phenomenon to the different current densities of 1 and 3 C, as shown in Figure 4d. The inset figures show the variation trend of discharge capacities under different current densities. Specifically, Ca$_9$Co$_{12}$O$_{28}$ delivers the reversible capacities of 1308, 595, 535, 474, 419, and 381 mA h g$^{-1}$ at 0.1, 0.5, 1, 2, 3, and 5 C, respectively. When the current density goes back to 0.1 C, the reversible capacities remain at around 608 mA h g$^{-1}$. In addition, Ca$_9$Co$_{12}$O$_{28}$ anodes deliver stable discharge capacities under different current densities, illustrating for their excellent rate capability.

For the energy storage materials, especially the anode materials of LIBs, the main problems are related to the fast capacity decay at high discharge rates. The possible reasons mainly include the structure collapse of electrode materials, aggregation of the nanoparticles, the significant volume variation, etc. However, in this article, the as-obtained bricklike Ca$_9$Co$_{12}$O$_{28}$ exhibits superior rate performance, which is superior to the most reported works (as shown in Table 1). The enhanced electrochemical performance can be attributed to the following factors: (a) the SDS surfactant can restrict the connection around the primary bricklike structures, thus controlling the particle sizes; (b) the stoichiometric metal ions are confined in the polymer gels, preventing the agglomeration of primary nanoparticles; (c) the comprehensive electrochemical properties of the system, including ionic/electronic conductivity, structural stability, etc., can be enhanced by the residual carbon layers on the surface, which are obtained from thermal decomposition of polymer chains; (d) in bricklike Ca$_9$Co$_{12}$O$_{28}$, rock salt CaO layers and CoO are alternately arranged along the c-axis direction. The inactive CaO matrix could alleviate the mechanical stress and the aggregation of metallic nanoparticles, whereas the active CoO offers good specific capacity, thus achieving synergistic effect.

### Table 1. Electrochemical Properties of the Reported Layered Co–Ca-Based Ternary Oxides for LIBs

| electrode description | synthesis method | specific capacity$^a$ | rate capability$^b$ | cycling stability$^c$ | refs |
|-----------------------|------------------|-----------------------|---------------------|----------------------|------|
| bricklike Ca$_9$Co$_{12}$O$_{28}$ | SDS-assisted Pechini process | 1287/1 C | 381/5 C | 517/200/1 C | our work |
| mixed oxides Ca$_3$Fe$_2$O$_5$ | high-temperature solid-state reaction | 722/10 mA/g | 183/50/60 mA/g | 15 |
| | solution method | 809/10 mA/g | 365/50/60 mA/g | | |
| Ca$_3$Co$_4$O$_7$ nanoflakes | citrate sol–gel method | 1230/0.5 C | 190/10 C | $\sim$500/50/0.5 C | 20 |
| Cr-doped Ca$_3$Co$_4$O$_7$ nanoplate | thermal hydrodecomposition method | $\sim$1000/0.1 C | 200/5 C | 513/100/0.1 C | 23 |
| porous Ca$_9$Co$_{12}$O$_{28}$ nanowires | low-temperature thermal decomposition | 541/0.1 C | 46/4 C | 256/190/1 C | 24 |
| Fe-doped Ca$_3$Co$_4$O$_9$ nanoflakes | citrate gel method | $\sim$1460/0.5 C | 241/10 C | 546/50/1 C | 36 |
| Ca$_9$Co$_{12}$O$_{28}$ nanoparticles | Pechini process | 816/200 mA/g | 210/50/200 mA/g | 13 |
| Ca$_9$Co$_{12}$O$_{28}$ multilayered | solid-state reaction | 762/200 mA/g | 141/50/200 mA/g | | |
| Ca$_9$Co$_{12}$O$_{28}$ microplates | | 790/200 mA/g | 151/50/200 mA/g | | |

$^a$Specific capacity [mA h g$^{-1}$] at various current densities. $^b$Rate capability [mA h g$^{-1}$] at high current density. $^c$Reversible capacity [mA h g$^{-1}$] remained after n cycles at certain current density.

12Co + 19Li$_2$O $\rightarrow$ 12CoO + 24Li + 7Li$_2$O (1st charge)

CoO + 2Li $\leftrightarrow$ Co + Li$_2$O (subsequent cycles)

On the basis of the first discharge reaction, the theoretical capacity of Ca$_9$Co$_{12}$O$_{28}$ is calculated to be 636 mA h g$^{-1}$ (38 Li per formula unit). However, a lower reversible capacity is obtained in the subsequent charge/discharge cycles (2 Li per formula unit). However, a lower reversible capacity is obtained in the subsequent charge/discharge cycles (2 Li per formula unit). This result can be attributed to the electrochemical inactivity of the CaO matrix.

As shown in Figure 4, in order to understand the electrochemical performance of Ca$_9$Co$_{12}$O$_{28}$ anode materials, we conduct further tests by coin-type batteries. The charge/discharge diagrams of the 1st, 20th, 50th, 80th, 100th, and 200th cycles at 1 C (C is defined as 38 Li per formula unit of Ca$_9$Co$_{12}$O$_{28}$) are shown in Figure 4a. The discharge capacity of the first cycle is up to 1287 mA h g$^{-1}$, which exceeds its theoretical value largely and reveals obvious capacity variation when proceeding to the following stages. We mainly attribute this phenomenon to the different reaction mechanism according to the as-mentioned equation and the formation of solid electrolyte interphase (SEI) surrounding active materials. In addition to that, the first discharge curve of the Ca$_9$Co$_{12}$O$_{28}$ anode can be mainly divided into three regions. In region (1), the voltage drops speedily to 0.71 V, which is related to the insertion of a small amount of lithium ions into Ca$_9$Co$_{12}$O$_{28}$. In regions (2) and (3), the voltage remains stable and then reflects a gradual voltage drop down to the cutoff voltage (0.001 V). These results correspond to the transformation of Ca$_9$Co$_{12}$O$_{28}$ into Co–CaO–Li$_2$O phases and the growth of the polymeric layer on the surface of the metal nanoparticles, respectively. From the 20th to 200th discharge curves, the voltage value of the plateau is around 1 V, higher than that of the 1st discharge curve. This may be ascribed to the conversion reaction from cobalt oxide to Co. The discharge capacities remain stable from the 20th to the 200th cycles, reaching 459, 472, 489, 497, and 517 mA h g$^{-1}$. The cyclic property of bricklike Ca$_9$Co$_{12}$O$_{28}$ is also evaluated under different current densities of 1 and 3 C, as shown in Figure 4b. Noticeably, the Ca$_9$Co$_{12}$O$_{28}$/Li half-cells undergo large irreversible capacity loss when proceeding to the second cycle because of the formation of SEI films and decomposition of Ca$_9$Co$_{12}$O$_{28}$ into the Co–CaO–Li$_2$O phase. During the following cycles, the capacity retention and Coulombic efficiency can remain at a high level even under the large rate of 3 C. After 200 cycles, the discharge capacities reach 517 and 392 mA h g$^{-1}$, while the Coulombic efficiencies are almost 100%. We can further observe the variation trend of Ca$_9$Co$_{12}$O$_{28}$ from the inset figures, which are selected from the discharge capacities of 2nd, 50th, 100th, 150th, and 200th cycles. Ca$_9$Co$_{12}$O$_{28}$ anodes experience almost no decline in discharge capability when the current rate increases from 0.5 C to 1 C. Under the high rate of 3 C, Ca$_9$Co$_{12}$O$_{28}$ anodes still show superior stability but sacrifice part of the reversible capacity. Figure 4c demonstrates the discharge curves of 0.5, 1, 2, and 3 C, from which we can observe a little decrease in specific capacities and working potentials. However, the small polarization at these current densities, especially at high current densities, demonstrates that the as-obtained samples own excellent ionic and electronic conductivities. Rate performance, as one of the significant factors for the practical application in EVs, has been evaluated as shown in Figure 4d.
4. CONCLUSIONS

Bricklike Ca₉Co₁₂O₂₈ mixed oxides are synthesized via a modified Pechini method with the assistance of the SDS surfactant. The as-obtained active/inactive nanocomposites are composed of highly dispersed Co nanoclusters embedded in the Li₂O–CaO matrix. Typically, Ca₉Co₁₂O₂₈ is used as a thermoelectric module. In our tentative use of it as an anode material in LIBs, we find its good electrochemical performance. Impressively, Ca₉Co₁₂O₂₈ can deliver the reversible capacity of 517 mA h g⁻¹ after 200 cycles at 1 C. Even under 3 C, the specific capacity still reaches 392 mA h g⁻¹ after 200 cycles. The Coulombic efficiencies are almost 100% under both rates. Inspiringly, this modified Pechini method can be potentially applied in the synthesis of other Co–Ca-based ternary oxides for electrochemical property improvement.

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Notes

The authors declare no competing financial interest.

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