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Surfactant-assisted crystallization of porous Mn₂O₃ anode materials for Li-ion batteries

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Abstract

MnCO₃ precursors with different morphologies were crystallized using three kinds of surfactants as soft template, i.e., cation surfactant cetyl trimethyl ammonium bromide (CTAB), anion surfactant sodium dodecyl sulfate (SDS) and neutral poly(vinyl pyrrolidone) (PVP). When PVP was used, the reaction manner was changed from only stirring at room temperature to hydrothermal route. Under hydrothermal conditions, different ethanol/water ratios and sources of CO_3^{2-} (NaHCO₃ and urea) were used. Porous cubic, regular spherical and nut-like spherical Mn₂O₃ samples can be obtained by the simple post-annealing process. The correlation between the morphology of Mn₂O₃ and its performance as anode material for Li-ion batteries was evaluated. The nut-like spherical Mn₂O₃ sample has the best cycling performance, with the specific discharge capacity of 925 mAh g⁻¹ at the current density of 100 mA g⁻¹ after 180 cycles. The sample composed of cube and sphere has superior rate performance. The

specific discharge capacity decreases with increasing the current density from ~ 872 mAh g⁻¹ at 100 mA g⁻¹ to ~ 361 mAh g⁻¹ at 2000 mA g⁻¹.

1. Introduction

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With the increasing demand for large-scale electrochemical energy storage, rechargeable lithium-ion batteries (LIBs) with a high energy density, high rate capability and long-term stability are urgently required.¹⁻⁶ Graphite, the commercial LIBs anode material, has relatively low Li storage capacity of 372 mAh g^{-1} .⁷ In order to meet the ever-growing performance demands, the search for alternative anode materials has become an urgent task.^{8,9} In recent years, nanostructured transition metal oxides have been attracting great interest as anode materials essentially because of their high theoretical specific capacity based on a novel conversion mechanism.¹⁰⁻¹⁴ Manganese oxide, including MnO, MnO₂, Mn₂O₃, and Mn₃O₄, is one of the most important metal oxide anodes because of its excellent electrochemical performance, low cost and environmental benign.¹⁵⁻²⁰ It is well-known that Mn₂O₃ possesses a high theoretical specific capacity (~1018 mAh g⁻¹) as an anode material for LIBs.^{21,22} However, like other transition metal oxides, Mn₂O₃ suffers from the volume expansion, aggregation, and intrinsically low conductivity during the cycling process, resulting in rapid capacity fading.^{23,24} To overcome these obstacles, different strategies have been usually proposed to resolve the aforementioned problems.²⁵⁻²⁷ Among them, the mostly used one is to synthesize Mn_2O_3 with porous or hollow structure. The vacant space provided by the hollow or porous structure can accommodate the

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structural strain and volume change, enlarge the contact area between the material and electrolyte, and shorten the diffusion path of Li ions during the Li ion insertion and extraction process.^{28,29}

Porous or hollow Mn₂O₃ is conventionally synthesized by a solid-state reaction through controlling thermal decomposition of precursors MnCO₃,³⁰⁻³³ Mn(OH)₂,³⁴ MnO₂³⁵ and Mn-complex³⁶. Porous Mn₂O₃ microspheres were synthesized by thermal treatment of MnCO₃ microspheres, which were synthesized as precursors by a hydrothermal method.^{30,31} Triple-shelled Mn₂O₃ hollow nanocubes were formed after the calcination of MnCO₃ nanocube.³² Hollow spheres, tubes, and lotus shapes of Mn₂O₃ were obtained after calcination of the corresponding MnCO₃, which were synthesized with the assistance of oxalic acid, tartaric acid and citric acid hydrothermally.³³ Porous Mn₂O₃ nanoflower and nanoplate were synthesized by thermal treatment of Mn(OH)₂.³⁴ Hollow Mn₂O₃ nanocones were synthesized by calcination of MnO₂ nanocone–CNTs composite to enable the conversion of MnO₂ to Mn₂O₃ and removal of CNTs simultaneously.³⁵ A simple post-annealing process of Mn-glycolate could form porous Mn₂O₃ nanoplates.³⁶

In this work, we compared the influences of addition of different surfactants (i.e., cation surfactant CTAB, anion surfactant SDS and neutral PVP) and the reactant concentration on the morphology of precursor $MnCO_3$, which will affect the morphology and thus electrochemical performance of Mn_2O_3 . To systematically study the influences of experimental parameters on the morphology of precursor $MnCO_3$, we employed different reaction manners including only stirring under room

temperature and hydrothermal method, different solvents and different alkali sources which offer CO_3^{2-} . The electrochemical properties of the as-prepared Mn_2O_3 were measured and the structure-property relationships were revealed.

2. Experimental

2.1 Materials preparation

All chemicals are of analytical grade (Kermel Co. Ltd. Tianjing, China) and used without further purification. Precursor MnCO₃ was synthesized by a precipitation or hydrothermal reaction. A precipitation reaction without using surfactant was conducted, and the obtained Mn₂O₃ sample had large particle size of several micrometers. Therefore, surfactant was used in our experiments to downsize the particles for improving the electrochemical performances. We chose three different surfactants: cation surfactant CTAB, anion surfactant SDS, and neutral PVP as soft template to compare their impact on the morphology of $MnCO_3$. In a typical synthesis, 0.8 g PVP (CTAB, SDS) was dissolved in 40 mL distilled water and stirred for 30 min. and then 8 mmol MnCl₂·4H₂O was added into the solution and stirred for another 30 min. At the same time, 9.6 mmol NaHCO₃ was dissolved into another 40 mL distilled water and stirred for 30 min to obtain another solution which was dropped into the above solution, and then the obtained mixed solution was stirred for 5 h. A white precipitate MnCO₃ was collected and washed with distilled water for several times and finally dried at 80 °C for 10 h. The obtained precursor MnCO₃ was sintered at 600 $^{\circ}$ C for 5 h with a ramping rate of 2 $^{\circ}$ C/min in air to prepare Mn₂O₃. The samples were

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named as S1 (PVP), S2 (CTAB) and S3 (SDS). In order to investigate the effect of reactant concentration on the morphology of MnCO₃, we also carried out the experiment that 0.8 g PVP was dissolved in 80 mL distilled water while other steps kept unchanged. The obtained sample was named as S4.

To study the effect of reaction manner, the mixed solution was transferred into a 100 mL Teflon linked autoclave and kept at 120 °C for 5 h instead of stirring under room temperature for 5 h. We also changed the solvent from 80 mL water to the mixed solvent of water and ethanol (40 mL water and 40 mL ethanol, 60 mL ethanol and 20 mL water) and used 40 mmol $CO(NH_2)_2$ instead of 9.6 mmol NaHCO₃. The obtained samples were named as S5–S8. The experimental parameters of S1–S8 were listed in Table 1.

2.2 Materials characterization

The crystal structure was analyzed by an X-ray diffraction (XRD) on a Rigaku SmartLab(9) diffractometer using CuK α X-rays at a scanning rate of 8° min⁻¹ between 10° and 80°. The tube voltage and current used were 45 kV and 200 mA, respectively. The size and morphology of samples were characterized using field-emission scanning electron microscopy (NOVA NanoSEM 450) at an accelerating voltage of 10.0 kV.

2.3 Electrochemical testing

To evaluate the electrochemical properties, 2025 coin type half-cells were fabricated. Batteries were assembled in argon atmosphere using lithium foil as cathode, cellgard 2300 as separator, 1M LiPF₆ in ethylene carbonate/dimethyl

carbonate/diethyl carbonate (EC/DMC/DEC, 1:1:1 vol %) as electrolyte and the synthesized Mn_2O_3 powders as anode materials. The anodes were fabricated by blade coating a mixture of synthesized powders, acetylene black, and polyvinylidene fluoride (PVDF) with a weight ratio of 70:20:10. A slurry of this mixture was made using NMP and was coated on a copper foil. After drying overnight at 80 °C, thin discs of 12 mm in diameter were punched and were used as anode. Galvanostatic charge–discharge tests were performed using a CT2001A cell tester (LAND Electronic Co. China). Rate capability was examined at different current densities from 100 to 2000 mA g⁻¹. Cyclic voltammetry was performed on a CHI660D electrochemical workstation between 3 V and 0.01 V at a sweep rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were also carried out using the same electrochemical workstation in the frequency range of 0.01 Hz–100 kHz.

3. Results and discussion

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The XRD patterns of the as-synthesized products were shown in Fig. 1. As can be seen from Fig. 1a, the patterns of the MnCO₃ precursors of S6 and S8 can be indexed as a pure rhombohedral structure (JCPDS Card No. 44-1472). From Fig. 1b, all Mn₂O₃ samples exhibit the same crystal structure corresponding to cubic Mn₂O₃ (JCPDS Card No. 2-896), and the sharp and strong peaks can well demonstrate good crystallinity and high purity of the samples.

Fig. 2a-h show the SEM images of S1–S8, respectively. The SEM images of Mn₂O₃ samples using different surfactants (S1: PVP; S2: CTAB; S3: SDS) are shown

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in Fig. 2a–c, and they are porous morphologies due to the thermal decomposition of the carbonate intermediate which releases CO₂. S2 and S3 have the particle size of $1-1.8 \mu m$, and S3 has hollow structure which can be seen from the fractured sphere. The morphology of S1 which used PVP as surfactant was porous spheres and cubes. The size of sphere is $1.8-3.5 \mu m$ and the size of cubes range from 800 nm to $1\mu m$. When decreasing the reactant concentration of S1, the proportion of cubes increases (S4, Fig. 2d), and the size of the sample decreased as a whole. This route was a chelating-agent-mediated solution-based synthetic route and was used for the synthesis of various shapes of MnCO₃ using PVP, CTAB, SDS as the chelating agents. It was observed that the binding strength and geometry of the chelating agent are the primary factors in determining which shapes were produced during the synthesis of MnCO₃.³³

For S5–S7, the reaction was conducted hydrothermally, and the amount of ethanol was 0 mL, 40 mL and 60 mL, separately. We found that the composition of the mixed solution had significant influence on the morphologies of the final products. As the amount of ethanol increased, the spherical morphology became loose and the particle size decreased. Herein, ethanol played a role in the growth process of crystals and used as shape-tuning agent and dispersant. The elevated pressure by increasing the amount of ethanol also enhanced the crystallization kinetics and afforded a driving force for the growth of small crystals.³⁷

When using 40 mL ethanol and 40 mL water as solvent and changing the source of CO_3^{2-} from NaHCO₃ to CO(NH₂)₂, the morphology changed from nut-like sphere

whose size was 500–600 nm to cube whose size was 5 μ m. Under hydrothermal conditions, alkali plays an important role in directing the reaction and crystallization, and the variety of alkali dramatically influences precipitate formation, crystal nucleation and growth process, ultimately leading to different morphologies of the products.³⁸ The lower hydrolysis rate of CO(NH₂)₂ compared to CO₃^{2–} resulted in slower MnCO₃ crystallization rate and then micron-sized MnCO₃ crystals were formed.

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In conclusion, the materials size can be controlled by changing the experimental parameters, such as the type of the surfactant, the concentration of the reactant, the reaction manner, the constitute of the solvent and the type of the alkali source. Using different surfactants can obtain samples with different morphologies and sizes. The particle size decreased as the concentration of the reactant decreased. When the reaction manner was changed from only stirring at room temperature to hydrothermal route, the particle size decreased due to the high crystallization rate under high pressure. Furthermore, the particle size continuously decreased when the molar ratio of ethanol/H₂O increased and it dramatically increased when using urea as alkali source instead of HCO_3^- due to the lower hydrolysis rate of $CO(NH_2)_2$ compared to HCO_3^- . Although the particle sizes of the samples are not too small, we can see from the SEM images that all Mn_2O_3 samples have porous structure. This unique structure facilitates Li^+ ion diffusion, thus making the conversion reaction reversible and leading to good conductivity.

Fig. 3a shows the first three successive scans of S6 in the voltage range of

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0.01-3.0 V and at a scanning rate of 0.1 mV s⁻¹. During the first scan, a broad cathodic peak centered around 1.16 V indicates the conversion of Mn³⁺ to Mn^{2+, 30,36} A second sharp cathodic peak observed at ~ 0.18 V originates from the conversion of Mn²⁺ to Mn⁰ along with the formation of Li₂O, and also from the irreversible reactions of organic carbonates in the electrolyte with Li at this low potential, forming a solid electrolyte interphase (SEI) layer.^{39,40} The minor peaks observed at ~0.94 V and 0.71 V may be due to the irreversible partial decomposition of the organic solvents. During the first anodic scan, only one relatively broad peak is observed at ~1.36 V, indicating the oxidation of Mn^0 to Mn^{2+} and partial decomposition of Li₂O to Li.^{30,36} Absence of any peak at higher voltages (up to 3.0 V) indicates no further oxidation of Mn. Consequently, in the subsequent cycles no peak is observed at 1.16 V during the cathodic scan. From the second cycle onwards, the CV curve consists of a single cathodic peak and the corresponding anodic peak due to the reversible conversion reaction $Mn^{2+} \leftrightarrow Mn^{0}$. However, a shifting of the peak position is observed for the cathodic process with reduction of peak intensity, which indicates that the irreversible reactions occurred during the first scan. Thus, the results of the CV are in perfect agreement with the reported electrochemical reaction of Mn_2O_3 based on the conversion mechanism:

$$2\mathrm{Li}^{+} + 3\mathrm{Mn}_{2}\mathrm{O}_{3} + 2\mathrm{e}^{-} \rightarrow 2\mathrm{Mn}_{3}\mathrm{O}_{4} + \mathrm{Li}_{2}\mathrm{O}$$
⁽¹⁾

$$2\mathrm{Li}^{+} + \mathrm{Mn}_{3}\mathrm{O}_{4} + 2\mathrm{e}^{-} \rightarrow 3\mathrm{MnO} + \mathrm{Li}_{2}\mathrm{O}$$
⁽²⁾

$$MnO + 2Li^{+} + 2e^{-} \leftrightarrow Li_{2}O + Mn$$
(3)

$$Mn + xLi_2O \leftrightarrow 2xLi^+ + MnO_x + 2xe^{-}(1.0 < x < 1.5)$$
(4)

The 2nd charge and discharge curves of S1–S8 at the rate of 100 mA g^{-1} are shown in Fig. 3b. The observed plateaus in the discharge and charge profiles of S1–S8 corroborate the CV observation for S6, and S3 shows lower specific capacity than other samples.

The cycling performance of the Mn₂O₃ samples prepared under different conditions were tested by galvanostatically charging/discharging the cells at a current density of 100 mA g^{-1} in the potential range between 0.01 and 3.0 V at room temperature. Fig. 4a shows the cycling curves of S1–S3. Their discharge capacities at the second cycle were 921 mAh g^{-1} , 808 mAh g^{-1} and 657 mAh g^{-1} , respectively. A fast capacity fading in the first 17 cycles was observed for S1 and S2, which may be attributed to the complicated side-reactions including the decomposition of electrolyte and irreversible phase changes of Mn₂O₃.³⁴ After the first 17 cycles, the capacities of S1 and S2 decreased to 720 mAh g^{-1} and 643 mAh g^{-1} , respectively. From 18th cycle on, the capacities started to increase, the maximum capacity of S1 was 803 mAh g^{-1} at 40th cycle and that of S2 was 766 mAh g^{-1} at 48th cycle. After the maximum capacity, the capacity started to decrease again. After 100 cycles, the capacities of S1 and S2 were 524 mAh g⁻¹ and 601 mAh g⁻¹, separately. Compared to S1 and S2, S3 had better cycle stability. After a fast capacity fading from 657 mAh g^{-1} to 550 mAh g^{-1} in the first 10 cycles, there was only 17 mAh g^{-1} loss in the following 90 cycles and the capacity was 533 mAh g⁻¹ after 100 cycles. The better capacity retention of S3 could be attributed to its hollow structure. As can be seen, the cycling data show wave-like shape. Although the mechanism behind the wave-like shape of capacity retention is

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not clear, some possible mechanisms have been proposed. The discharge capacity loss can be attributed to the large specific volume change during lithiation and delithiation.³³ The further increasement of the discharge capacity may be caused by the presence of a possible activation process in the electrode, which is commonly observed for transition metal oxides.³² By comparing the electrochemical performances of S1–S3, we can see that the sample using PVP as surfactant had largest initial capacity, but its cycle stability was worst. In order to improve its cycling performance, different experiments were conducted, such as changing the concentration of the reactant, the manner of reaction, the constitute of the solvent and the type of the alkali under hydrothermal conditions.

The cycling performances of S1 and S4 are shown in Fig. 4b to study the effect of the reactant concentration. When the concentration of the reactant decreased, S4 had larger capacity than S1, however, the changing trend of capacity for S4 was similar to that of S1. After a fast capacity fading from 893 mAh g⁻¹ to 777 mAh g⁻¹ in the first 10 cycles, the capacity started to increase, and the maximum capacity of S4 was 1068 mAh g⁻¹ at 51th cycle, which was slightly larger than the theoretical specific capacity (~1018 mAh g⁻¹) of Mn₂O₃ and the excess capacity could be associated with the decomposition of the electrolyte at low voltages generating an SEI layer and the further lithium storage via interfacial charging at the metal–Li₂O interface.⁴¹ After the maximum capacity, the capacity decreased slightly. After 180 cycles, its capacity was 739 mAh g⁻¹. The larger capacity of S4 than S1 could be attributed to the larger proportion of cube in S4, which has smaller size than the sphere.

The cycling performances of the Mn_2O_3 samples prepared under hydrothermal conditions using different mixed solvents are shown in Fig. 4c. S6 had the largest initial capacity of 959 mAh g⁻¹ among the three samples, however, its capacity decreased slightly. On the contrary, the capacity of S7 increased gradually. From 55th to 135th cycle, the capacity of S7 was larger than S6. Although both S6 and S7 had nut-like spherical morphology, the structure of S7 was looser than S6, which would facilitate the diffusion of Li⁺ ions. However, from 135th circle on, the capacity of S7 was larger than S7, which may be attributed to the collapse of the structure of S7 under long time charge/discharge. The specific discharge capacity of S6 was 925 mAh g⁻¹ after 180 cycles. S5 had the smallest capacity in the whole cycles with an initial capacity of 819 mAhg⁻¹, and it decreased to 618 mAh g⁻¹ at 100th cycle. The reasons why S5 had the smallest capacity among the three samples may be due to its largest particle size, which resulted in smallest contact area with electrolyte.

The cycling performances of the Mn_2O_3 samples using different source of CO_3^{2-} and the mixed solvent of 40 mL ethanol and 40 mL water under hydrothermal conditions are shown in Fig. 4d. Compared to S6, S8 had smaller capacity because of its larger particle size and smaller contact area with electrolyte. For S8, after a fast capacity fading from 768 mAh g⁻¹ to 454 mAh g⁻¹ in the first 20 cycles, there was no obvious capacity fading in the following 80 cycles, and the capacity decreased to 400 mAh g⁻¹ at 100th cycle.

The rate capability of the porous S4, S6 and S7 were also evaluated at different

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current densities as shown in Fig. 5a. As expected, the specific discharge capacity of

S4 decreased with current density from ~872 mAh g^{-1} at 100 mA g^{-1} to ~493 mAh g^{-1}

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at 1000 mA g^{-1} . Even at a current density of 2000 mA g^{-1} , the specific capacity was

 \sim 361 mAh g⁻¹. At larger current density, the diffusion of lithium ion is accelerated, which cause them cannot react with the electroactive material promptly.³⁵ When the current density was decreased from 2000 back to 100 mA g^{-1} , ~933 mAh g^{-1} was recovered. This shows that S4 had capacity retention capability and good rate performance. Compared to S4, S6 had worse rate performance. Its specific discharge capacity decreased with increasing current density from ~903 mAh g^{-1} at 100 mA g^{-1} to ~433 mAh g^{-1} at 1000 mA g^{-1} . When the current density increased to 2000 mA g^{-1} , the specific capacity decreased to ~ 279 mAh g⁻¹. However, the specific capacity increased to ~960 mAh g^{-1} when the current density returned to 100 mA g^{-1} . We could see that although S4 had better rate performance than S6, their capacity retention capabilities were identical. Among the three samples, S7 had the worst rate performance. Its specific discharge capacity decreased from \sim 752 mAh g⁻¹ to \sim 212 mAh g^{-1} when the current density increased from 100 mA g^{-1} to 2000 mA g^{-1} , and ~ 818 mAh g^{-1} was recovered when the current density returned to 100 mA g^{-1} . Such difference of the rate performance was considered to be caused by their electrochemical reaction resistance. Fig. 5b shows the representative charge and discharge curves of Mn_2O_3 (S4) anode at various current densities. The discharge potential decreases and the charge potential increases with increasing the charge-discharge rate, which is due to the kinetic effects of the material, and this

indicates a good kinetic feature and facile charge transport process under high rates.⁴²

Fig. 5c shows the Nyquist plots of S4, S6 and S7 at room temperature in the frequency range of 100 kHz to 0.01 Hz when using fresh cells. They have the same shapes of Nyquist plots, composed of one semicircle component at high frequency and followed by a linear component at the low frequency. Obviously, S4 has the smallest semicircle among the three samples, which means that S4 has the smallest electrochemical reaction resistance. A small electrochemical reaction resistance was beneficial to improve the conductivity of the electrode and enhance the reaction kinetics, resulting in a better cycle and rate performance.^{43,44}

4. Conclusions

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In summary, we crystallized Mn_2O_3 with different sizes and shapes via both stirring at room temperature and hydrothermal route. Electrochemical performances of these samples demonstrate that Li-ion storage capacity and cycling behavior of Mn_2O_3 are strongly influenced by its shape and size. Both regular spheres and fractured hollow spheres were respectively obtained when using CTAB and SDS. The samples using PVP as surfactant have both cubic and spherical morphologies. When decreasing the reactant concentration, the proportion of cube increases and the 100th specific discharge capacity increases from 522 mAh g⁻¹ to 841 mAh g⁻¹. The samples using NaHCO₃ as alkali source under hydrothermal condition are regular sphere, compacted and loose nut-like spheres when the proportion of ethanol in the mixed solvent increases. When using urea as alkali source, cubic micron-sized crystal with the size of 5 μ m was obtained. Nut-like spherical S6 has the best cycling performance, and the specific discharge capacity was 925 mAh g⁻¹ after 180 cycles. The rate performance of S4 composed of cube and sphere is the best, and the specific discharge capacity decreases with increasing current density from ~872 mAh g⁻¹ at 100 mA g⁻¹ to ~361 mAh g⁻¹ at 2000 mA g⁻¹.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21401017, 51125009), the Fundamental Research Funds for the Central Universities (Grant No. DUT13LK17), the Scientific Research Fund of Liaoning Provincial Education Department (Grant No. L2013030), the Open Project of State Key Laboratory of Rare Earth Resources Utilization (Grant No. RERU2013013), and the Hundred Talents Program of Chinese Academy of Sciences.

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Samples	Surfactant	MnCl ₂	NaHCO ₃ /urea	Solvent	Reaction manner*
S 1	0.8 g PVP	8 mmol	9.6 mmol NaHCO3	80 mL H ₂ O	Stirring
S2	0.8 g CTAB	8 mmol	9.6 mmol NaHCO ₃	80 mL H ₂ O	Stirring
S3	0.8 g SDS	8 mmol	9.6 mmol NaHCO ₃	80 mL H ₂ O	Stirring
S4	0.8 g PVP	8 mmol	9.6 mmol NaHCO ₃	$120\ mL\ H_2O$	Stirring
S5	0.8 g PVP	8 mmol	9.6 mmol NaHCO ₃	80 mL H ₂ O	Hydrothermal
S6	0.8 g PVP	8 mmol	9.6 mmol NaHCO ₃	40 mL H ₂ O, 40 mL ethanol	Hydrothermal
S7	0.8 g PVP	8 mmol	9.6 mmol NaHCO ₃	20 mL H ₂ O, 60 mL ethanol	Hydrothermal
S8	0.8 g PVP	8 mmol	40 mmol urea	40 mL H ₂ O, 40 mL ethanol	Hydrothermal

* "Stirring" implies stirring for 5 h under room temperature; "Hydrothermal" implies

hydrothermal treatment under 120 $^{\circ}\text{C}$ for 5 h.



Fig. 1. (a) XRD patterns of $MnCO_3$ precursors of S6 using NaHCO₃ as alkali and S8 using urea as alkali; (b) XRD patterns of Mn_2O_3 samples S1–S8. The standard patterns of $MnCO_3$ (JCPDS 44-1472) and Mn_2O_3 (JCPDS 2-896) are shown for reference.



Fig. 2. FESEM images of samples S1–S8 (a–h).



Fig. 3. (a) The initial three consecutive CVs of the Mn_2O_3 electrode (S6) in the voltage range of 0.01–3.0 V versus Li⁺/Li at a scan rate of 0.1 mV s⁻¹; (b) The 2th discharge–charge profiles for S1–S8.



Fig. 4. Cycling performance of (a) S1–S3, (b) S1 and S4, (c) S5–S7, (d) S6 and S8.



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Fig. 5. (a) Rate performance of S4, S6 and S7 at different current densities from 100 to 2000 mA g^{-1} ; (b) The representative charge and discharge curves of Mn_2O_3 (S4) anode at various current densities; (c) Nyquist plots of S4, S6 and S7 in the frequency range of 100 kHz to 0.01 Hz when using fresh cells.

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Graphical abstract



High performance porous Mn₂O₃ anode materials for Li-ion batteries were prepared

by surfactant-assisted crystallization.