Na_{0.44}MnO₂ with very fast sodium diffusion and stable cycling synthesized via polyvinylpyrrolidone-combustion method

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Abstract: Na_{0.44}MnO₂ is a very promising cathode material in sodium-ion batteries for large-scale application. Na_{0.44}MnO₂ with very fast sodium diffusion and stable cycling is prepared by polyvinylpyrrolidone (PVP)-combustion method. X-ray diffraction, scanning electron microscope and high-resolution transmission electron microscopy are conducted to explore the morphology and structure. Electrochemical performance of the samples is examined in coin cells with sodium foil anode and

nonaqueous electrolyte. The $\text{Na}_{0.44}\text{MnO}_2$ sample synthesized at 900 °C (NMO-900) discharges the highest capacity of 122.9 mAh g⁻¹ at C/5. A fast-rate-test technique developed by Newman *et al.* is adopted for quick determination of the rate capability. All the samples exhibit good rate capability while the NMO-900 shows the best. Normal rate test result supports the reliability of the fast rate test. Even at 20 C charge and discharge rate, the NMO-900 delivers 99 mAh g⁻¹ capacity. The chemical diffusion coefficient of sodium is measured to be around 3×10^{-12} cm² s⁻¹ by potential intermittent titration technique (PITT). The cycling stability is also very good. The capacity retention after 100 cycles at 1 C is 87.9% and the capacity still remains 82.9% even after 700 cycles at 10 C. During cycling the coulombic efficiency keeps near 99.8%.

Key words: Sodium-ion battery; Sodium manganese oxide; Cathode material; High power; Sodium chemical diffusion coefficient; Polyvinylpyrrolidone

1. Introduction

Nowadays, various energy storage systems have been studied for application in portable electronic devices, electric vehicles and smart electric grids. While lithium-ion batteries are currently the premier energy storage system for portable electronics and electric vehicles because of their superior power and energy density [1]. For large grid-scale application, the limited resource availability of lithium and

future high cost will be problems and arouse much debate [2-6]. As a result, sodium-ion batteries (abbr. SIB or NIB) are currently under consideration as options for large scale energy storage coupled to renewable energy sources, due to the huge availability of sodium, its low price and the similarity of both Li and Na insertion chemistries [7, 8]. The researches on electrode materials for SIB have been revitalized and reviewed by ref. [9, 10].

Intrinsically, the large size of Na^+ (1.02 Å) relative to Li^+ (0.69 Å) and the lower ion-ion Coulomb repulsion for Na^+ should cause slower solid-state diffusion and lead to inferior power ability [11, 12].

Therefore electrode materials with large-size diffusive tunnels for Na^+ ions should be favorable for fast solid diffusion. There are various cathode materials for SIB reported in literature, such as olivine phosphates [13-16], fluorophosphates [17-20], NASICON (Na^+ super ionic conductor) related compounds [21], sodium metal oxides[22-32], and Prussian blue analogues [33-38]. Among these potential cathode materials, tunnel-structured orthorhombic $\text{Na}_{0.44}\text{MnO}_2$ (abbr. NMO) is particularly attractive because its crystal structure forms large-size tunnels and can tolerate some stress for sodium de/inversion (Fig. 1). It has a theoretical specific capacity of 121 mAh g^{-1} when cycled between 4 V and 2 V in the sodium position of 0.22 to 0.66. Besides, its intrinsic electronic conductivity is reported to be $10^{-6} \text{ S cm}^{-1}$ [39], a moderate value for practical use, which means in practice not too much extra efforts are needed to further improve its intrinsic conductivity [40]. The special crystal structure means orthorhombic $\text{Na}_{0.44}\text{MnO}_2$ should possess high rate capability and stable cycle stability as a cathode material.

M. Doeff *et al.* [41, 42] reported Na_xMnO_2 as a cathode material for SIB firstly. F. Sauvage *et al.* [43] prepared pure rod-like $\text{Na}_{0.44}\text{MnO}_2$ samples and carefully studied the insertion/deinsertion mechanism of sodium into $\text{Na}_{0.44}\text{MnO}_2$. Cao *et al.* [44] reported $\text{Na}_{0.44}\text{MnO}_2$ nanowires prepared with a polymer-pyrolysis method which have good cycling performance. However, the rate capability of reported $\text{Na}_{0.44}\text{MnO}_2$ samples needs to be improved considering the structure [45, 46]. H. Zhou *et al.* [22] prepared nanowires with a high surface area of $28.2 \text{ m}^2 \text{ g}^{-1}$ by hydrothermal method. The nanowire cathode in an optimized cell structure with 45 wt% acetylene black as conductive additive delivered 115 mAh g^{-1} at 0.42 C rate and 103 mAh g^{-1} at 8.3 C rate. Y.-M. Chiang *et al.* [47] supposed the low-rate scenarios for NMO cells reported in the literature are possibly due to low conductivity of the electrolytes or slow charge transfer at the active material/electrolyte interface, and successfully prepared high power $\text{NaTi}_2(\text{PO}_4)_3/\text{Na}_{0.44}\text{MnO}_2$ aqueous sodium ion batteries with micro-sized $\text{Na}_{0.44}\text{MnO}_2$.

We believe that the sodium diffusion in NMO particles is also an important factor for the rate capability. The previous reported sodium chemical diffusion coefficient in $\text{Na}_{0.44}\text{MnO}_2$ is rather low [44, 46, 48], which seems in contradiction with the large-size tunnels in the material. If $\text{Na}_{0.44}\text{MnO}_2$ with much faster sodium diffusion is prepared by appropriate synthesis method, it could be supposed that NMO will also have good rate capability with nonaqueous electrolyte.

In this paper, single-crystalline, micro-sized $\text{Na}_{0.44}\text{MnO}_2$ with very fast sodium diffusion and stable cycling was prepared by a PVP-combustion method. A

fast-rate-test technique is adopted for quick determination of the rate capability and is compared with normal test method for the prepared NMO as a cathode material with sodium foil and nonaqueous electrolyte. The sodium chemical diffusion coefficient is measured by potential intermittent titration technique (PITT).

2. Experimental

2.1. $\text{Na}_{0.44}\text{MnO}_2$ Synthesis

$\text{Na}_{0.44}\text{MnO}_2$ was prepared by poly (vinyl pyrrolidone) (PVP) -assisted gel combustion method. In detail, NaHCO_3 , $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (Na : Mn = 0.44 : 1), and PVP (the molar ratio of PVP monomer to total metal ions was 2.0) were dissolved in deionized water and pH = 3 was achieved by adding 1:1 HNO_3 . The mixture was stirred at 120 °C to obtain dried gel. The dried gel was ignited on a hot plate to induce a combustion process which lasted for several minutes. The resulting precursor was preheated at 400 °C for 2 h and then calcined at 850 °C, 900 °C or 950 °C (denoted as NMO-850, NMO-900 and NMO-950, respectively) for 6 h with the heating rate of 5 °C min⁻¹. After heat treatment, the oven was switched off and the sample was cooled down naturally. The whole process was performed in air.

2.2. Morphology and crystal structure characterization

The analysis of the phase purity and the structural characterization were made by X-ray powder diffraction (XRD) using a Bruker D2 PHASER diffractometer equipped with Cu K α radiation that was operated over a 2θ range of 10~70° in a continuous scan mode with a step size of 0.004°. The morphology was examined

using a JEOL 7500F scanning electron microscope (SEM). High-resolution transmission electron microscopy (HRTEM) analysis was carried out *via* a Philips CM200FEG at the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory (LBNL) and the acceleration voltage was 200 kV.

2.3. Electrochemical tests

The $\text{Na}_{0.44}\text{MnO}_2$ cathode was prepared by mixing 80 wt.% active material, 10 wt.% acetylene black (AB) and 10 wt.% polyvinylidene fluoride (PVdF) binder in N-methylpyrrolidone (NMP) to form a slurry. The slurry was doctor-bladed onto aluminum foil, dried at 60 °C, and then punched into electrode discs with a diameter of 12.7 mm. The prepared electrodes were dried at 130 °C for 12 h in a vacuum oven and show typically an active material loading of about 2 mg. The electrochemical cells were fabricated with the $\text{Na}_{0.44}\text{MnO}_2$ cathode, sodium foil anode, 1 mol L⁻¹ NaClO_4 in propylene carbonate (PC) as electrolyte, and glass fiber as separator in an argon-filled glove box. Electrochemical performances were evaluated using CR2325 coin cells. Galvanostatic charge-discharge tests were performed using Maccor 4000. The potential intermittent titration technique (PITT) test were conducted using Bio-Logic VMP-3 multichannel electrochemical Analyzer.

3. Results and dsicussion

3.1. Synthesis and characterization

The XRD patterns of the as-prepared $\text{Na}_{0.44}\text{MnO}_2$ are displayed in Fig. 2. The patterns confirm the formation of well-crystallized $\text{Na}_{0.44}\text{MnO}_2$ (JCPDS No. 27-0750).

The NMO synthesized at 850 °C shows some Mn_2O_3 impurity [44, 45]. When the calcination temperature increases to 900 °C or 950 °C, all diffraction peaks can be indexed as an orthorhombic structure and *Pbam* space group. The cell parameters (Table 1) are well consistent to the previously reported results [22, 43, 46, 47]. The patterns of NMO-900 has the sharpest peaks and the ratio of peaks intensity agrees with the reported results best [47].

The SEM and HR-TEM images of the $\text{Na}_{0.44}\text{MnO}_2$ are showed in Fig. 3. Most of the as-prepared $\text{Na}_{0.44}\text{MnO}_2$ particles are rod shaped and well crystallized. HR-TEM images of all the samples show ordered one-dimension lattice and suggest single-crystalline structure. There are some differences in the shape of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at different temperatures. The NMO-850 particles contain many small irregular particles and the rod-shaped particles are short. When the calcination temperature increases, the small irregular particles become less and the rods become longer. The length and width distributions of the rod-shaped particles at different calcination temperature are counted from 150~200 particles in lower magnification SEM images (Supplementary Fig. S1, Fig. S2 and Fig. S3) and are showed in Fig. 4. It is clearly seen that the length of NMO-900 particles is higher than that of NMO-850 particles, but the length of NMO-900 and NMO-950 particles are near. However, the width of NMO-850 and NMO-900 particles are near and a little lower than that of NMO-950 particles. The statistics suggest the $\text{Na}_{0.44}\text{MnO}_2$ particles grow along axial direction from 850 °C to 900 °C and grow along radial direction from 900 °C to 950 °C.

3.2. Galvanostatic charging and discharging characteristics at C/5

It is well known that there are three sodium sites (referenced as Na1 Na2 and Na3 in Fig. 1). Na1 and Na2 are situated in large S-shaped tunnels, which are half occupied while another site (Na3) is in smaller tunnels which are fully occupied [43]. Therefore, the reaction equation for charge and discharge of $\text{Na}_{0.44}\text{MnO}_2$ is

Theoretically, the first charge capacity of $\text{Na}_{0.44}\text{MnO}_2$ is a half of its first discharge, then the second charge and discharge show its full capacity. Fig. 5 exhibits the second charge and discharge curves of the $\text{Na}_{0.44}\text{MnO}_2$ at C/5. The discharge capacities of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at 850 °C, 900 °C and 950 °C are 116.0 mAh g⁻¹, 122.9 mAh g⁻¹ and 117.9 mAh g⁻¹, respectively. The NMO-900 shows the highest capacity. The coulombic efficiencies in the second cycle of NMO-850, NMO-900 and NMO-950 are 98.3%, 98.6% and 99.1%, respectively. The increase of coulombic efficiency along the calcination temperature increasing is due to slighter side reactions caused by lower specific surface area at higher calcination temperature. The coulombic efficiencies at the second cycle for all the samples are higher than reported values [44, 46]. There are many voltage plateaus corresponding to the peaks in dQ/dV curves (Fig. 6). The dQ/dV curves are rather complicated. It is still not clear what reactions refer to theses peaks. The dQ/dV curves of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at different temperatures do not show much difference. The peaks are sharp and well split. The difference of the redox peaks near 3.2 V is only 25 mV, which suggests the low impedance and good reversibility. The dQ/dV curves for NMO-900 show higher

intensity at peak a and b, which may be the origin of its higher capacity than NMO-850 and NMO-950.

3.3. Rate tests

A fast-rate-test technique developed by Newman *et al.* [49] is adopted for quick determination of the rate capability for the as-prepared NMO. Although the model is based on lithium ion batteries, it could be also applicable to sodium system. As shown in Fig.7a, the cells are charged at C/10 to 4.0 V firstly, then they are discharged at 20 C to 2.0 V. After 5 min rest, the cells' voltage is higher than 2.0 V, then they are discharged at 10 C. In the same way, the rest and discharge alternate at 5 C, 1 C, C/2, C/5 and C/10. The capacity during 20 C discharge plus that during 10 C corresponds to the capacity for 10 C in normal charge-discharge test. The "20 C + 10 C +5 C" capacity corresponds to the capacity for 5 C in normal charge-discharge test, and so on. The fast rate test for every sample was repeated 3 times to check the repeatability. It can be seen the repeatability is good from Fig. 7 b-d. Fig. e & f show the rate capabilities of NMO-900 and NMO-950 are very similar, while the rate capability of NMO-850 is lower. Even at 20 C, the NMO-900 and NMO-950 still deliver over 80% capacity. It's the highest value up to now.

The excellent rate capability originates from the large S-shape tunnels which allow Na⁺ ions intercalate and deintercalate quickly. On the other hand, the synthesis method is important to form Na_{0.44}MnO₂ with homogeneous mixture, ordered lattice and uniform crystallinity which can exhibit its intrinsic rate capability. Previously, we have shown that the PVP-assisted combustion is a successful method to synthesize

LiMn₂O₄ nanoparticles [50, 51], large micrometer-sized LiMn₂O₄ [52], and LiNi_{0.5}Mn_{1.5}O₄ [53, 54] with very excellent electrochemistry performance. The PVP combustion method provides a precursor solution with homogeneous distribution of the constituents at the atomic level for the Na⁺ and Mn²⁺ ions can be strongly chelated by the amide groups on the polymeric chains. In addition, different from normal polymer pyrolysis process, the precursor containing PVP and NO₃⁻ is pyrolyzed violently and therefore burns quickly when it is heated. PVP has been widely used as an excellent shape-control agent for metal colloids. It acts as a stabilizing agent, preventing aggregation of metal particles and retaining a uniform colloidal dispersion [55]. Although the exact function of PVP in this gel-combustion method needs further study, we believe PVP can also separate the Na_{0.44}MnO₂ particles during pyrolysis and help the crystal grow homogeneously in the calcination. Thereby micro-sized particles with good electrochemistry performance can be obtained with this method.

To confirm the reliability of the above method, normal rate test for NMO-900 was also adopted, as shown in Fig. 8. The error between the two kinds of method at every C-rate is below 1.5%, so the values in Fig.7 is highly accurate corresponding to normal rate-test method. In additional, the capacities still remain high when charge and discharge are both 5C, 10C and 20C. Even at 20C charge and discharge rate, the NMO-900 delivers 99 mAh g⁻¹ capacity. This result indicate that Na_{0.44}MnO₂ is able to not only discharge quickly but also charge quickly. When the rate recover to 1C, the capacity recover 99.8% compared to the capacity at the last cycle of the first 1C

procedure. It suggests that the $\text{Na}_{0.44}\text{MnO}_2$ keeps its structure stable even after suffering very high rate charge-discharge.

3.4. Sodium diffusion studies

In previous reports, the sodium chemical diffusion coefficient (D_{Na^+}) of $\text{Na}_{0.44}\text{MnO}_2$ is as low as 10^{-14} to $10^{-16} \text{ cm}^2 \text{ s}^{-1}$ accompanying with rather low rate capability [44, 46, 48]. Y.-M. Chiang *et al.* [47] argued that fast diffusion and phase transformation should be possible in this material considering abundant vacancies for Na^+ ion diffusion in the S-shape tunnel and possible strain accommodation upon Na^+ ion extraction/insertion. To confirm this opinion, and study the reason for the good rate capability of the $\text{Na}_{0.44}\text{MnO}_2$ prepared *via* PVP combustion method, the sodium chemical diffusion coefficient (D_{Na^+}) was determined by potential intermittent titration technique (PITT). In the PITT experiments, a small potential step size (20 mV) and a low enough cutoff current (C/50) were adopted to ensure the equilibrium states were achieved at every potential step. Then the sodium chemical diffusion coefficient, D_{Na^+} , can be calculated from the slope of the linear region in the $\ln I(t)$ vs. t plot, as defined in equation (2) [56]:

$$D_{\text{Na}^+} = -\frac{d \ln(I)}{dt} \frac{4L^2}{\pi^2} \quad (2)$$

where I is the current in the potential step and L is the diameter of a spherical particle. In this application, the particles are rod like so the quadratic mean of width is used to substitute the L value. The values of D_{Na^+} measured from PITT and the potential plotted with sodium content are shown in Fig. 9. The sodium diffusion values vary considerably with concentration from $1.5 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ to $2.7 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ which

are much higher than previous reports and comparable with LiMn_2O_4 [57]. From 2 V to 3.46 V, the D_{Na^+} values vary around $3 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ with small amplitude. This result proves that sodium diffusion in $\text{Na}_{0.44}\text{MnO}_2$ is fast.

3.5. Cycling stability tests

The cycling stability of NMO-900 was tested at 1 C and 10 C (both charge and discharge rate) and showed in Fig. 9. The NMO-900 shows excellent cycling stability at both 1 C and 10 C. The capacity retention at 1 C after 100 cycles is 87.9% while the capacity still remain 82.9% even after 700 cycles at 10 C. It is noticed that the cycling stability at 1 C is worse than that at 10 C. The reason may be that capacity fading depends on not only cycling but also time. The mechanism of the capacity fading of $\text{Na}_{0.44}\text{MnO}_2$ is still under studying and will be discussed in future works. The coulombic efficiencies at 1 C and 10 C are both near 99.8 during cycling. At 10 C, it even over 99.9% after the 200th cycle. The high coulombic efficiency during cycling is very important for cycling performance when this material is used as cathode material in full batteries [58, 59].

4. Conclusions

Single-crystalline $\text{Na}_{0.44}\text{MnO}_2$ with very high rate capability and cycling stability was synthesized *via* PVP-combustion method. The $\text{Na}_{0.44}\text{MnO}_2$ calcined at 900 °C shows the highest capacity of 122.9 mAh g^{-1} at C/5 and the best rate capability. At 20 C charge and discharge rate, this material delivers 99 mAh g^{-1} capacity. The sodium

chemical diffusion coefficient is as high as $3 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ which is comparable with LiMn_2O_4 . Thus, in this paper we prove that Na^+ ion diffuses fast in $\text{Na}_{0.44}\text{MnO}_2$ based on the theoretical analysis of its structure. The cycling stability is also very good. The capacity retention at 1 C after 100 cycles is 87.9% while the capacity still remain 82.9% even after 700 cycles at 10 C. During cycling the coulombic efficiency keeps near 99.8%. The results in this paper suggest that $\text{Na}_{0.44}\text{MnO}_2$ is a promising candidate for the applications which need high power, high life and low cost batteries, such as energy storage power station or HEV.

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Table 1 Cell parameters of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at 850 °C, 900 °C and 950 °C.

Sample	a	b	c
NMO-850	9.101(4)	26.41(1)	2.818(2)
NMO-900	9.080(3)	26.37(1)	2.827(1)
NMO-950	9.093(4)	26.36(1)	2.821(2)

Fig captions

Fig. 1. Schematic crystal structure of $\text{Na}_{0.44}\text{MnO}_2$ perpendicular to the *ab* plane

Fig. 2. XRD patterns of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at 850 °C, 900 °C and 950 °C.

Fig. 3. SEM (left) and HR-TEM (right) images of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at

850 °C, 900 °C and 950 °C.

Fig. 4. The length and width distributions of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at 850 °C, 900 °C and 950 °C.

Fig. 5. The second charge and discharge curves of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at 850 °C, 900 °C and 950 °C. The charge and discharge rate is C/5.

Fig. 6. The dQ/dV curves of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at 850 °C, 900 °C and 950 °C in the second cycle. The charge and discharge rate is C/5.

Fig. 7. Fast-rate-test results of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at 850 °C, 900 °C and 950 °C. a. Diagram of the fast rate test. b-d. Specific capacity vs. C-rate in 3 cycles of NMO-850, NMO-900 and NMO-950. e. Specific capacity vs. C-rate at the 3rd cycle of the three samples. f. Capacity percentage relative to C/10 vs. C-rate at the 3rd cycle of the three samples.

Fig. 8. The normal rate test result of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at 900 °C.

Fig. 9. Voltage curve during PITT test and the calculated diffusion coefficient of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at 900 °C.

Fig. 10. Cycling stability and coulombic efficiency during cycling of the $\text{Na}_{0.44}\text{MnO}_2$ synthesized at 900 °C. a. Charge and discharge rate is 1 C. b. Charge and discharge rate is 10 C

Figure

Figure1

Figure2

Figure3

Figure4

Figure5

Figure6

Figure7

Figure8

Figure9

Figure10a

Figure10b