1.3 V superwide potential window sponsored by Na-Mn-O plates as cathodes towards aqueous rechargeable sodium-ion batteries

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Abstract

Aqueous rechargeable sodium-ion batteries (ARSIBs) are highly desirable for the large-scale energy storage due to their inherent high safety and low-cost. Na-Mn-O electrode material has been considered as a promising cathode, yet the redox potential window is still not fully explored and utilized in aqueous rechargeable sodium-ion batteries. Herein, a chemical bonded $\text{Na}_{0.44}\text{MnO}_2$ (NMO) plates are successfully synthesized *via* a polyvinylpyrrolidone-assisted sol-gel route followed by annealing process. The possibility of utilizing a wider potential window ranging between -0.3 V to 1.0 V *vs.* Ag/AgCl in mild aqueous electrolyte has been thus demonstrated by using NMO plates as cathodes for the first time. As a result, the as-synthesized NMO plates can deliver a highest initial discharge capacity of 77.2 mA h g^{-1} at a current density of 100 mA g^{-1} , compared with previous Na-Mn-O reports in mild aqueous electrolyte in ARSIBs. Even at a high rate of 500 mA g^{-1} , it still maintains a large capacity of 35 mA h g^{-1} after 1000 cycles, demonstrating its superior cycling stability. In addition, *ex-situ* SEM and TEM-EDX results reveal that there is a newly formed sheet-like layer Na-birnessite $\text{Na}_{0.55}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ on the surface of NMO cathodes, which can provide extra ion channel for sodium ions and stabilize the electrode from pulverization, resulting in improved cycling stability. This study provides a broad implication for developing low-cost, high performance cathode materials to broaden the applied potential window towards high performance ARSIBs.

Keywords

Aqueous rechargeable sodium-ion batteries; widened potential window; $\text{Na}_{0.44}\text{MnO}_2$; cathode material

In this advance technological era, there has been an increasing demand for safe, economical and sustainable energy storage system [1-5]. Since Dahn *et al* first introduced the aqueous lithium-ion based batteries using $\text{LiMn}_2\text{O}_4//\text{VO}_2(\text{B})$ in aqueous electrolyte, research efforts have been directed on the aqueous based rechargeable batteries (ARBs) ever since [6-12]. The main advantages of adopting ARB systems is the substitution of highly expensive and flammable carbonated based electrolyte with low cost aqueous-based electrolyte [6-15] and the improved ionic conductivity afforded by such water based solvents [16-19].

The first ARSIB on the other hand was proposed by Whitacre *et al*, using Na-Mn-O cathodes to harness the relative abundance and low cost of sodium [11-13]. According to the previous studies, NMO is an attractive candidate as cathode materials because of the presence of large S-shaped and O-shaped pentagonal tunnels, which can facilitate facile sodium migration from the host structure [20-23]. However, in ARSIB systems reported previously, NMO was cycled in a narrower potential range between 0 V to 0.7 V *vs.* Ag/AgCl (corresponding to 2.9 V to 3.6 V *vs.* Na/Na⁺) as compared to that of non-aqueous system [21] (2.0 V to 4.0 V *vs.* Na/Na⁺), which resulted in a reduced discharge capacity of around 40 mA h g⁻¹ (corresponding to 0.15 mol of Na) at a current density of 25 mA g⁻¹ [12, 14]. Such a shortcoming is notably hindering the development of NMO cathodes for the real applications in ARSIBs [11-13, 21].

Recently, research efforts in tuning the electrolyte (e.g. “water-in-salt” sodium-ion based electrolyte) with expanded potential window [24, 25] and using alkaline electrolyte in dual-ion system coupled with zinc as anode [26], have suggested the obvious improvement towards the aqueous rechargeable battery performances. However, the high cost of the electrolyte used still hinders its practical application. Therefore, it would be a more cost-effective approach to work on the suitable material

processing of NMO with expectation of superior cycling stability in a wider potential window in ARSIBs.

In this work, we demonstrated that constructing a chemical bonded microstructure between NMO plates enables the as-obtained NMO cathodes to be stable in a 1.3 V superwide potential window in mild aqueous electrolyte in ARSIBs. The NMO plates were first fabricated *via* a PVP-assisted sol-gel method followed by a high-temperature annealing process at 900 °C. Then, we demonstrated the possibility of utilizing a wider potential window which allows a higher de/insertion of sodium content (0.28 mol). Specifically, the electrochemical reversibility of NMO was evaluated by adjusting the discharge cut-off voltage (-0.8 V to -0.3 V) to gain in-depth understanding of the redox behaviour. As a result, the NMO plates as cathode presents the superior electrochemical performance with a highest capacity of 77.2 mA h g⁻¹, compared to that of control samples (NMO rods, 73.5; NMO particulates, 67.2) and Na-Mn-O reported in mild aqueous electrolyte in ARSIBs [9, 10, 12, 14]. Moreover, even at a high current density of 500 mA g⁻¹, NMO plates exhibit excellent electrochemical stability with a discharge capacity of 35 mA h g⁻¹ after 1000 cycles. Notably, *ex-situ* scanning electron microscopy (SEM) and transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (TEM-EDX) analysis reveal that a sheet-like Na-birnessite layer is formed on the surface of NMO plates electrode during the cycling process, which can serve as a protective layer to stabilize the electrode from pulverization and thus significantly enhancing the cycling stability during the long-term cycling.

The crystal structures of as-prepared products are confirmed by high energy X-ray powder diffraction (XRD). As shown in Fig. 1a, all the diffraction peaks of NMO samples can be indexed to orthorhombic Na_{0.44}MnO₂ phase (PDF: 04-018-3147) with

a space group $Pbam$, which is in good agreement with previous report [27]. The sharp diffraction peaks indicate the high crystallinity of the as-synthesized NMO products. A Rietveld structure refinement of X-ray powder diffraction data has been performed, as shown in Fig. S1, the structure lattice parameters of NMO plates are $a = 9.0841(6) \text{ \AA}$, $b = 26.408(1) \text{ \AA}$, $c = 2.8238(2) \text{ \AA}$, with a lattice volume of $677.42(7) \text{ \AA}^3$. Fig. 1b shows the specific crystal structure of NMO products. The respective polyhedral are connected to each other by corner and edge sharing which form O-shaped and S-shaped tunnels that can provide three de/insertion sites (Na 1, Na 2 and Na 3) for sodium-ions along the c-axis [20, 21, 28-30]. Fig. 1c-e show the SEM images of the as-obtained NMO samples. It can be observed that inhomogeneous particulates were synthesized *via* solid-state reaction (Fig. 1c). In contrast, uniform plates with lengths of $3.0\text{--}7.7 \text{ \mu m}$ and widths of $1.8\text{--}6 \text{ \mu m}$ were successfully yielded by employing PVP-assisted sol-gel method (Fig. 1d). Meanwhile, decreasing the annealing temperature can render the morphology transformation of plates to rods (lengths of $5\text{--}8 \text{ \mu m}$ and widths of $0.2\text{--}0.5 \text{ \mu m}$), as shown in Fig. 1e. The uniform growth of plates and rods are attributed to the interaction between imide groups of PVP and metal ions, which can prevent agglomeration, facilitate nucleation process and effectively stabilize the particle growth [31-33].

To further examine the microstructure of the as-prepared product, the NMO plates are investigated by TEM. Fig. 2a presents a low magnification TEM image of NMO plates. It can be seen that NMO plates are composed of a series of flakes bundled together. HRTEM image in Fig. 2b clearly shows that well-defined lattice fringes with interplanar spacing of 0.28 nm and 0.26 nm correspond well to (001) and $(0\ 10\ 0)$ crystal planes of NMO, respectively, well matching with XRD results. This further confirm the highly ordered crystals arrangement of NMO with crystal growth along

the [001] plane direction. The anisotropic formation of plates structure is possibly due to the faster crystal growth along [001] direction than other directions based on the unique orthorhombic lattice structure of NMO [34]. The magnified TEM image in Fig. 2c further confirms that several adherent flakes overlaying each other to form slab-like NMO plates. Notably, the slab-like structure is constructed by parallel plates without obvious grain-boundary from each other. It cannot only enable stable electrode upon cycling, but also provide open [001] channels for fast sodium ion diffusion [20, 28]. Besides, the lattice fringes with same interplanar spacing of 0.45 nm, corresponding to (200) plane, can be clearly observed from the adjacent flakes (Fig. 2d). The result demonstrates that the flakes further crystallize, chemical bonded with each other during the heating process, forming a very well interlaced structure, which can reduce the sodium ion diffusion barrier and improve the electrochemical polarization [20, 28, 35].

Cyclic voltammetry (CV) measurements were recorded to probe the reversibility and electrode kinetics of the as-obtained NMO plates in both aqueous and non-aqueous electrolytes. In non-aqueous electrolyte, the reversible redox potential window for NMO plates falls between 2.0 V to 4.0 V *vs.* Na/Na⁺ and it can achieve a high discharge capacity of 104.3 mA h g⁻¹ at a current density of 100 mA g⁻¹ as shown in Fig. S2 and S3. In comparison, when tested in mild aqueous electrolyte, a superwide reversible redox potential window is demonstrated between -0.3 V to 1.2 V *vs.* Ag/AgCl *via* adjusting discharge cut-off voltage. Fig. 3a depicts the CV curves of NMO plates electrode at the first, second and fifth cycles. It can be clearly observed that NMO plates electrode exhibits five sharp reversible redox peaks (labelled as I-V) during the oxidation and reduction process in mild aqueous electrolyte (Fig. 3a). These peaks correspond to the complex multiphase transition of sodium-ions de/insertion

[20, 21, 34, 36]. The specific redox peak potential and corresponding sodium-ions de/insertion sites are summarized in Table S1. Specifically, the pair of redox peaks III corresponds to the Na-ions insertion/extraction of O-shaped tunnel (Na 1 site) while the other pairs of redox peaks I, II, IV, and V correspond to de/insertion of Na-ions in the larger S-shaped tunnel (Na 2 and 3 sites) [21]. In addition, the peaks in the fifth cycle nearly overlap with those in the second cycle, demonstrating the good reversibility of NMO plates electrode in the wide potential window. Moreover, Fig. S4 shows the CV curves of NMO plates measured at three potential ranges with different discharge cut-off voltage. When cycled to potential of -0.4 V vs. Ag/AgCl, the NMO plates have begun to exhibit irreversible redox behaviour located at redox peaks IV and V. This is possibly due to the structural distortion of S-shaped tunnel with the de/insertion of sodium-ions. Furthermore, the irreversible redox behaviour becomes more obvious when potential is taken to -0.8 V vs. Ag/AgCl. Specifically, there is a large irreversible reduction peak located at -0.55 V vs. Ag/AgCl, caused by the dissolution of Mn^{2+} into the aqueous electrolyte [28]. Meanwhile, we compare the potential window and electrochemical performance of our NMO plates with other reported Na-Mn-O in ARSIB literatures. As shown in Fig. 3b and Table S2, our NMO plates for the first time demonstrates a highly reversible intercalation behaviour (-0.3 V to 1.0 V vs. Ag/AgCl) in mild aqueous electrolyte coupled with a much higher discharge capacity (77.2 mA h g^{-1} at a current density of 100 mA g^{-1}) than those reported Na-Mn-O in ARSIB literatures [9, 10, 12, 14].

Fig. 4a depicts the 2nd galvanostatic discharge/charge (GCD) profiles of NMO plates, rods and particulates at a current density of 100 mA g^{-1} . Specifically, the plateaus in the discharge profiles of NMO plates are attributed to sodium-ions insertion into host structure [21], which is well consistent with the CV result. In

general, the discharge/charge potential difference is related to the electrode polarization in electrochemical reactions. Notably, the polarization of NMO plates electrode is remarkably low among the three samples, which can be ascribed to the unique chemical bonded plates structure.

Fig. 4b compares the cycling performance of NMO plates, rods and particulates at 100 mA g⁻¹. It can be clearly seen that NMO particulates electrode suffers serious capacity fading during the initial cycles, which indicates its instability within this wide potential window. Compared to that of particulates, both plates and rods exhibit better cycling stability. Among them, NMO plates electrode delivers the highest initial discharge capacity of 77.2 mA h g⁻¹ (corresponding to 0.28 mol Na⁺) and an excellent cycling stability with a capacity of 60.1 mA h g⁻¹ after 100 cycles. This can be attributed to the unique chemical bonded plates structure, which can facilitate the (de-) intercalation of sodium ions and help release strains resulting from sodium-ions insertion/extraction as compared to that of aggregated bulk particulates in the wide potential window. This is by far, to our best knowledge, the highest capacity achieved by Na-Mn-O electrodes in mild aqueous electrolyte in ARSIBs when compared to previous reports as compiled in Table S1 [9, 10, 12, 14].

In addition to the high capacity and enhanced cycling stability, the NMO plates show superior rate capability which is much better than that of particulates and rods. As shown in Fig. 4c, the NMO plates can deliver discharge capacities of 83.5, 62.6, 59.1, 56.7, and 51.3 mA h g⁻¹ at various current densities from 25, 50, 100, 200 to 500 mA g⁻¹. When the current density is back to 25 mA g⁻¹, the capacity can recover to 75 mA h g⁻¹, suggesting its excellent electrochemical performance of NMO plates.

To obtain further understanding of the different electrochemical behaviours, electrochemical impedance spectroscopy (EIS) measurements were conducted on the

NMO pristine and after 100 cycles samples at a current density of 100 mA g⁻¹. Fig. S5 presents the Nyquist plots and the corresponding fitted equivalent circuit (inset of Fig. S5). Both Nyquist plots display similar profile with a semicircle at high-medium frequency region and a sloping straight line at low-frequency region, indicating the charge transfer and ion diffusion electrochemical behaviour, respectively. Table S3 presents the charge transfer resistance at interfaces (R_{ct}) values of NMO samples before and after 100 cycles. It is noteworthy that the R_{ct} values of NMO plates and rods electrodes decrease as the cycles proceed as compared to that of NMO particulates. This is possibly due to the fragmentation and agglomeration of the particulates, which will lead to poor connection of the electrode material and current collector, resulting in an increased R_{ct} . Specifically, the R_{ct} value of NMO plates (3.7 Ω) after cycling is much smaller than that of NMO rods (6.4 Ω) and particulates (20.6 Ω), indicating an excellent electrical conductivity of NMO plates, which results in superior electrochemical properties.

In addition to R_{ct} , the apparent Na⁺ diffusion coefficient D_{Na+} can be estimated from the inclined line in the Warburg region using the following equation [37]:

$$D = R^2 T^2 / (2 A^2 n^4 F^4 C^2 \sigma^2)$$

where R is the universal gas constant, T is the absolute temperature, A is the surface area of the electrode, n is the number of transferred electrons per molecule during reduction, F is the Faraday constant (96500 C mol⁻¹), C is the sodium ions concentration in the electrode (9.81×10⁻³ mol cm⁻³) [14, 38], and σ is the Warburg coefficient associated with Z_{re} ($Z_{re} \propto \sigma \omega^{1/2}$). Fig. 4d presents the linear relationship between Z_{re} and $\omega^{1/2}$ in the low-frequency region. The value of σ can be obtained by the slope of fitted line. Thus, the calculated D_{Na+} value of NMO plates is 4.69×10⁻¹²

$\text{cm}^2 \text{ s}^{-1}$, higher than that of rods ($4.43 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) and particulates ($2.2 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$), indicating the enhanced sodium-ion diffusion kinetics of NMO plates.

It is well known that long-term charge-discharge cycling is another key indicator for real application of ARSIBs. To identify the long-term cyclic stability at high rate of the NMO plates, the cell was tested up to 1000 cycles at a high rate of 500 mA g^{-1} (with a prior 10 cycles at a current density of 50 mA g^{-1}) as shown in Fig. 4e. NMO plates can retain a high capacity of 35 mA h g^{-1} after 1000 cycles, indicating good structural stability and excellent electrochemical reaction kinetics. This result further demonstrates the superior long-term cycling stability of NMO plates, thus presenting as a promising cathode for practical applications.

To gain further insight into the structural evolution upon cycling, the *ex-situ* SEM measurement was performed. In Fig. 5a, b and c, it can be observed that the NMO plates and rods electrodes still maintain uniform plates and rods morphologies after 100 cycles, while NMO particulates possess agglomerates of fragmentized particles. Notably, newly formed sheet-like structures are also observed on the top surface of cycled NMO plates and rods electrode (Fig. 5d and e) when compared to that of pristine electrodes (Fig. S6a and b). However, this phenomenon cannot be detected in the cycled NMO particulates electrode (Fig. 5f and S6c). The sheet-like structure of cycled NMO plates electrode is further confirmed by the *ex-situ* TEM image as shown in Fig. 6a. In addition, TEM coupled energy dispersive X-ray spectroscopy (TEM-EDX) analysis indicates that the nanosheet-like structure consists of Na, Mn and O elements (Fig. 6b). The Cu and C elements come from the TEM grid. The high-resolution TEM (HRTEM) image in Fig. 6c shows lattice fringes with spacing of 0.25 nm , which may correspond to the (200) plane of Na-birnessite. The selected area electron diffraction (SAED) pattern in Fig. 6d exhibits three diffraction rings, which

could be assigned to the (200), (004) and (31-1) planes of Na-birnessite $\text{Na}_{0.55}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ (JCPDS No.43-1456) [39, 40]. As a result, the newly formed Na-birnessite with a sheet-like structures on the surface of NMO plates upon cycling can provide more sodium intercalation sites and help stabilize the electrode from pulverization. Due to the reduced side reaction inhibited by this layer [39, 40], unique chemical bonded plates structure and fast sodium-ion diffusion, the NMO plates can achieve excellent cycling stability and good rate capability. The formation mechanism of the layer on cycled NMO plates electrodes will be further investigated in the later publication.

In summary, the 1.3 V superwide applicable potential window (-0.3 V to 1.0 V vs. Ag/AgCl) for $\text{Na}_{0.44}\text{MnO}_2$ plates in mild aqueous electrolyte has been demonstrated in ARSIBs for the first time. Benefiting from the synergistic effects of wide potential window, unique chemical bonded plates structure and fast sodium-ion diffusion, the as-prepared NMO plates display superior electrochemical properties with high capacity, good rate capability and excellent long-term cycling stability. Furthermore, sheet-like Na-birnessite layer detected on the surface of NMO plates electrodes upon cycling, is found to be another contributing factor towards better cycling stability. This study offers a new pathway for developing low-cost, high performance cathode materials to broaden the applicable potential window towards high performance aqueous rechargeable sodium-ion batteries.

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Conflicts of interest

The authors declare no conflict of interest.

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Figure captions

Fig. 1. (a) XRD patterns of NMO samples, (b) crystal structure of $\text{Na}_{0.44}\text{MnO}_2$, SEM images of NMO particulates (c), plates (d) and rods (e).

Fig. 2. (a, c) TEM and (b, d) HRTEM images of as-prepared NMO plates.

Fig. 3. (a) Cyclic voltammetry (CV) curves of NMO plates electrodes at the first, second and fifth cycles in 1M Na_2SO_4 electrolyte at a scan rate of 0.1 mV s^{-1} , (b) comparison of potential window and electrochemical performances of our NMO plates and other Na-Mn-O electrodes in previous ARSIBs literatures.

Fig. 4. (a) 2nd galvanostatic charge and discharge (GCD) curves of NMO plates, rods and particulates at a current density of 100 mA g^{-1} , (b) cycling and (c) rate performances of NMO electrodes, (d) linear fits of the Z_{re} vs. $\omega^{-1/2}$ curves of the NMO electrodes in the low-frequency region, and (e) long-term cycling performance of NMO plates at a high current density of 500 mA g^{-1} .

Fig. 5. SEM images taken on the cross section and top view of the cycled NMO electrodes (a, d) plates, (b, e) rods and (c, f) particulates. The corresponding magnified images are inset of Fig. 5d, e and f.

Fig. 6. (a) TEM image, (b) EDX analysis, (c) HRTEM image and (d) SAED pattern of the layer on the surface of the cycled NMO plates electrode.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6 **Highlights**

- A 1.3 V superwide potential window for $\text{Na}_{0.44}\text{MnO}_2$ in mild aqueous electrolyte has been demonstrated for the first time.
- The $\text{Na}_{0.44}\text{MnO}_2$ plates exhibit high capacity and superior cycling stability.
- A sheet-like layer has been observed on cycled NMO plates electrode.
- The Na-birnessite layer can enhance cycling stability.