



Non-layer-transformed Mn_3O_4 cathode unlocks optimal aqueous magnesium-ion storage via synergizing amorphous ion channels and grain refinement

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ABSTRACT

Aqueous rechargeable magnesium ion batteries (ARMBs) have obtained more attention due to the two-electrons transfer nature, low cost and safety. However, the scarcity of cathode materials seriously hinders the development of ARMBs because of the unfavorable strong interaction between Mg^{2+} and cathode material. Herein, we choose a pre-treated spinel Mn_3O_4 cathode for aqueous Mg^{2+} storage. The pre-treatment in Na_2SO_4 solution induces the grain refinement decorated with tortuous amorphous ion diffusion channels, facilitating the production of electrochemical reaction active sites and the diffusion of Mg^{2+} , respectively, which achieve a (sub-)surface pseudocapacitance reaction between Mn (II) and Mn (III). As a result, the pre-treated Mn_3O_4 cathode exhibits a package of optimal performances, i.e., a capacity of 98.9 mAh g^{-1} and a high capacity retention rate of 99.4% after 2000 cycles. To the best of our knowledge, our work not only provides a new reaction mechanism of spinel Mn_3O_4 in aqueous batteries system, but also affords a high cycle stability electrode material for rechargeable Mg^{2+} energy storage.

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1. Introduction

Towards highly efficient energy storage, higher energy density and safer devices are urgently needed, e.g., dual-ion batteries or aqueous batteries [1–5]. Aqueous rechargeable magnesium ion batteries (ARMBs), as one of multivalent metal ion batteries, have attracted more concern since the conductive ions have capacity to transfer two electrons, leading to higher energy density than monovalent ion batteries (such as lithium ion battery) [6–8]. In addition, ARMBs are considered as one of the most promising batteries due to the relatively high volumetric capacity (3833 mAh cm^{-3}), low reduction potential (2.4 V vs. SHE), low cost and high safety [9–13].

However, the current research on ARMBs is still immature concerning the lack of choice of cathode materials. Due to the bivalence of Mg^{2+} , the Coulombic interaction between Mg^{2+} and electrode material itself is relatively strong, which leads to a greater resistance to the intercalation and diffusion process of

Mg^{2+} in the electrode material [14–16]. Thus, Mg^{2+} cannot easily escape from electrode material to achieve a completely reversible electrochemical reaction, which in turn leads to capacity decay and poor cycling stability [17–19]. To the best of our knowledge, the common Mg^{2+} storage mechanism is the insertion/extraction of Mg^{2+} ion [6,8,20] or phase conversion reaction [11,21]. The former is hindered by the diffusion of Mg^{2+} in cathode materials, and the latter causes great structural damage. As a consequence of both the occurrence, it leads to poor cycle stability and long-cycle capacity retention. In order to address the scarcity of cathode material for Mg^{2+} ion batteries, the cathode materials of lithium ion batteries (or further processing) are often used to storage Mg^{2+} because the radius of Mg^{2+} is approaching to the Li^+ one. Shan et al. [22] exploited FePO_4/C prepared via electrochemical delithiation of LiFePO_4/C as a cathode material for ARMBs, which attained 21 mAh g^{-1} at 1C (the theoretical value is 164 mAh g^{-1}). Nevertheless, due to the strong Mg^{2+} interactions among the adjacent channels, the difference in rates occurs for Mg^{2+} insertion and extraction. Besides, the cathode materials with large ion diffusion channels are also the promising options for Mg^{2+} ion batteries. Zhang et al. [23] obtained microsheet morphology of todorokite-type magnesium manganese oxide molecular sieve (Mg-OMS-1)

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material. It shows a good battery behavior for Mg^{2+} insertion/extraction in aqueous electrolyte, which exhibited a discharge capacity of $\sim 75 \text{ mAh g}^{-1}$ at 0.2 A g^{-1} and a specific capacity retention rate of 83.7% after cycling 300 cycles at 0.1 A g^{-1} . However, such cathode material for Mg^{2+} storage has low specific capacity and poor structural stability, which cannot meet the requirements of high-performance energy storage. Therefore, searching for a cathode material with high reversible capacity and superior cycle stability is an urgent need for rechargeable aqueous batteries.

It is known that spinel Mn_3O_4 (141/amd) is constructed by the basic unit of MnO_6 octahedra with corner- and/or edges-sharing manners. The Mn (II) and Mn (III) occupy tetrahedral (8a) and octahedral (16d) sites, respectively [24,25]. Spinel Mn_3O_4 is generally used as a cathode material in lithium ion organic battery, and the main reaction mechanism is described as $\text{Mn}_3\text{O}_4 \leftrightarrow \text{MnO} \leftrightarrow \text{Mn}$ [26]. Whereas, such spinel Mn_3O_4 usually transforms to a layered birnessite MnO_2 for subsequent electrochemical reactions in aqueous battery system [21,27,28]. There are no reports, to the best of our knowledge, to experimentally and theoretically the possibility for a direct electrochemical energy storage of Mn_3O_4 as cathode material in aqueous battery.

In this work, we not only demonstrate spinel Mn_3O_4 used as cathode for storing Mg^{2+} , but also show a simple pre-treated method to enhance both the Mg^{2+} and electron transports in spinel Mn_3O_4 . Our pre-treated Mn_3O_4 in Na_2SO_4 induced a hybrid of amorphization and grain refinement (about a reduction with one magnitude of order). The amorphization enables the fast diffusion of Mg^{2+} and buffers the volume changes of Mg^{2+} insertion into the crystalline Mn_3O_4 . In addition, such grain refinement shortens the diffusion distance of Mg^{2+} , electron transfer and exposes more active sites. As a consequence, our pre-treated Mn_3O_4 achieves fast and reversible redox reaction between Mn (II) and Mn (III) with Mg^{2+} insertion and extraction, exhibiting a high specific discharge capacity of 98.9 mAh g^{-1} and excellent capacity retention rate of $\sim 99.4\%$ after 2000 cycles at a current density of 0.2 A g^{-1} . For the first time, our work not only offers a new energy storage mechanism of spinel Mn_3O_4 in aqueous electrolyte, but also produces a cathode material for ARMBs with high long cycle capacity retention rate.

2. Experimental

2.1. Chemicals

Manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium sulfate anhydrous (Na_2SO_4), magnesium sulfate anhydrous (MgSO_4) were purchased from Aladdin. Ethanol absolute, Graphite powder and Nafion were purchased from Sino-pharm Chemical Reagent Co., Ltd, Alfa Aesar and Dupont, respectively. All these materials were used in subsequent reactions without further purification. The carbon fiber paper was purchased from Sigma-Aldrich, and subsequently cut into a size of $1 \times 1 \text{ cm}^2$.

2.2. Synthesis of Mn_3O_4 -I nanoparticles

Mn_3O_4 -I Nanoparticles were prepared through a simple precipitation reaction. NaOH (1 g) was dissolved into 50 mL deionized water, and then slowly added dropwise to the solution formed by dissolving MnSO_4 (0.8451 g) in 200 mL of deionized water under vigorous stirring. The resulting suspension was stirred for 24 h and let stand until it separated. The precipitates obtained were gathered, washed with water and ethanol for three times and dried at 60°C for 12 h to obtain Mn_3O_4 nanoparticles.

2.3. Synthesis of Mn_3O_4 -I cathode

Mn_3O_4 was mixed with Nafion (5 wt%) and Graphite powder in a mass ratio of 70:15:15 with ethanol. The mixture was stirred to a homogenous slurry with a magnetic bar for 12 h. Next, the slurry was coated onto carbon paper ($1 \times 1.5 \text{ cm}^2$) and drying at 60°C for 12 h. This is named as Mn_3O_4 -I (Initial).

2.4. Synthesis of Mn_3O_4 -A cathode

Mn_3O_4 -A Cathode was prepared through electrochemical Cyclic Voltammetry (CV) at a scan rate of 0.025 V s^{-1} for 200 cycles at 0–1.3 V (vs. SCE) in 0.5 M Na_2SO_4 electrolyte.

2.5. Characterization

X-ray diffraction (XRD) measurements were performed (equipped with Cu K_α radiation, $\lambda = 1.5418 \text{ \AA}$) on a Rigaku D/max2600 X-ray diffractometer. Scanning electron microscopy (SEM, Hitachi SU8010) and energy dispersive X-ray spectroscopy (EDS) were used to characterize the morphology and size statistics diagrams. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were conducted for phase analysis using a JEM-2100F electron microscope. X-ray photoelectron spectroscopy (XPS) was carried out using a K_α X-ray spectrometer (ThermoFisher Scientific Company) with an Al source, and the standard binding energy of C 1s is 284.8 eV . Raman analysis was conducted using TESCAN RISE (S9000G). RISE (Raman Imaging and Secondary Electron Microscopy) gives the information about both the morphology and structure of the same regions [29].

The sample for *ex-situ* XRD in Fig. 1(a) was the same electrode as the one at different cycle number at the scan rate of 0.025 V s^{-1} in 0.5 M Na_2SO_4 solution in three-electrode system. Before the XRD, the filter papers were used to absorb the moisture on the surface of electrode. Another *ex-situ* XRD test sample adopts also the same electrode as the one stopped at different potential by GCD at the current density of 0.02 A g^{-1} . The *ex-situ* XPS samples were cut from a larger electrode with the CV cycles at the scan rate of 0.001 V s^{-1} at different potentials.

2.6. Electrochemical measurements

CV and galvanostatic charge/discharge measurement (GCD) were conducted using CHI660E electrochemical workstation. Electrochemical impedance spectroscopy was performed by PARSTAT 2273. The as-prepared Mn_3O_4 -A cathodes was tested in three-electrode system with Pt foil and SCE as counter and reference electrodes, respectively. The electrolyte was 1 M MgSO_4 aqueous solution.

3. Results and discussion

3.1. Structural characterization

The nanoparticles before pre-treatment is named Mn_3O_4 -I (Mn_3O_4 -Initial). The as-prepared Mn_3O_4 was later pasted onto carbon fiber paper and underwent CV cycles in 0.5 M Na_2SO_4 at a scan rate of 0.025 V s^{-1} . The one at 200th cycle is named Mn_3O_4 -A (Mn_3O_4 -Activated).

XRD pattern of the sample was presented in Fig. S1, in which almost all the characteristic peaks were indexed to tetragonal hausmannite Mn_3O_4 (JCPDS No. 24–0734) [27,30,31]. *Ex-situ* XRD (Fig. 1a) was used to identify the structural transformation of electrode material during the CV process. With the increased electrochemical activation, no changes have been found for the XRD

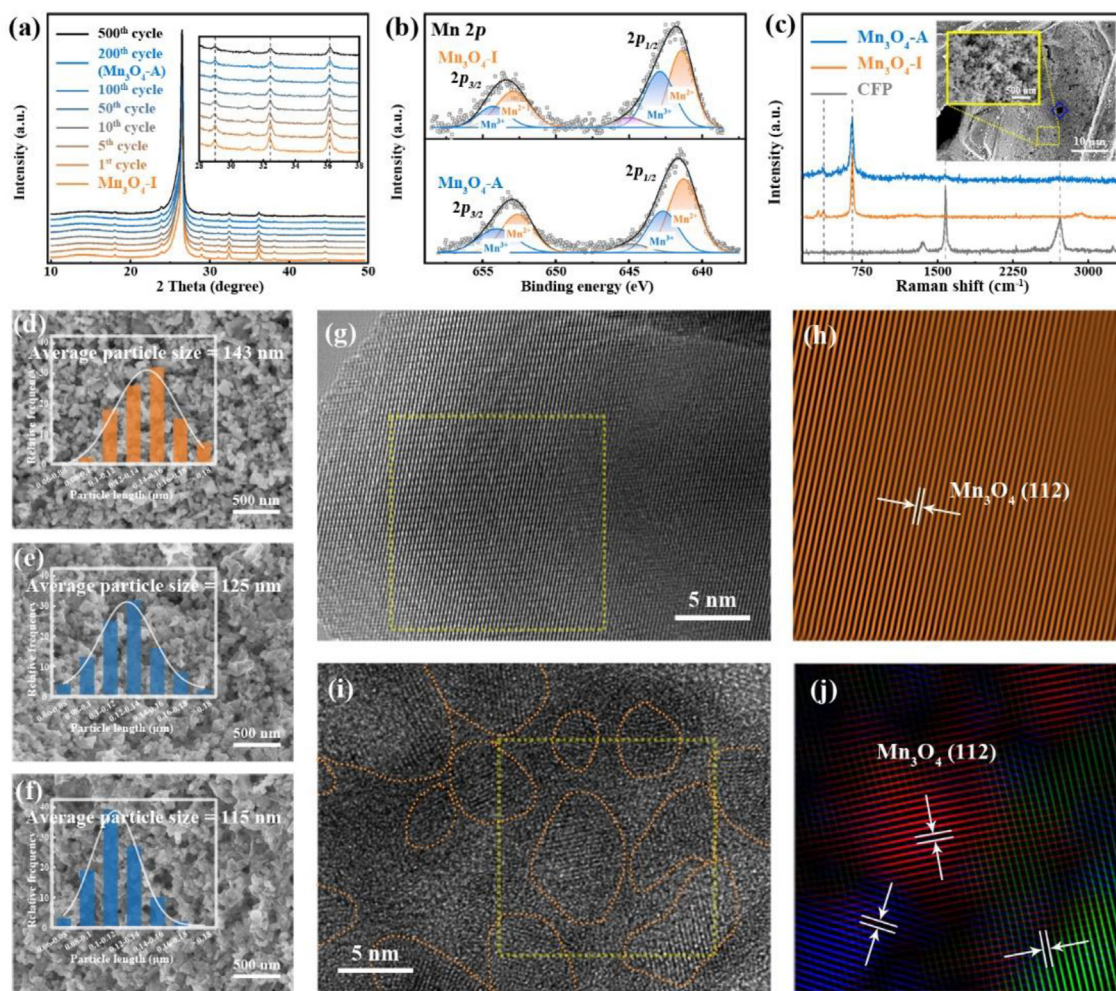


Fig. 1. Structural characterization of $\text{Mn}_3\text{O}_4\text{-I}$ and $\text{Mn}_3\text{O}_4\text{-A}$. (a) *Ex-situ* XRD patterns of electrode at different CV cycles at a rate of 25 mV s^{-1} . (b) XPS of Mn 2p $\text{Mn}_3\text{O}_4\text{-I}$ and $\text{Mn}_3\text{O}_4\text{-A}$. (c) RISE (Raman imaging and secondary electron microscopy) image and spectra of $\text{Mn}_3\text{O}_4\text{-A}$ and Raman spectra of $\text{Mn}_3\text{O}_4\text{-I}$ and carbon paper. (d–f) SEM images and size statistics diagrams of nanoparticles in CV at 0th cycle, 100th cycle and 200th cycle. (g–j) HRTEM image and inverse fast Fourier Transform (IFFT) of $\text{Mn}_3\text{O}_4\text{-I}$ and $\text{Mn}_3\text{O}_4\text{-A}$.

peaks. The intensity of XRD peaks assigned to spinel Mn_3O_4 decreased gradually along with the increases of CV cycles. However, no further change occurred after 200 cycles. In addition, they are quite similar for the XRD peak of 500th and 200th cycles, indicating that the structure tended to be stable after 200 cycles. That is to say, there was no phase transformation of spinel Mn_3O_4 in the process of pre-treatment.

Mn 2p XPS spectra of $\text{Mn}_3\text{O}_4\text{-I}$ and $\text{Mn}_3\text{O}_4\text{-A}$ were presented in Fig. 1(b). The peaks centered at the binding energies of ~ 641.3 and $\sim 652.7 \text{ eV}$ belonged to Mn $2p_{1/2}$ and $2p_{3/2}$ of Mn (II) in Mn_3O_4 , respectively. The peaks centered at the binding energies of ~ 642.8 and $\sim 654 \text{ eV}$ were attributed to Mn $2p_{1/2}$ and $2p_{3/2}$ of Mn (III) in Mn_3O_4 , respectively. The peak located at the binding energy of $\sim 644.9 \text{ eV}$ was assigned to Mn $2p_{1/2}$ of Mn (IV) in Mn_3O_4 [32]. The peak area ratios of Mn (II), Mn (III) and Mn (IV) were 52%, 30% and 18% in $\text{Mn}_3\text{O}_4\text{-I}$ and 55%, 28% and 17% in $\text{Mn}_3\text{O}_4\text{-A}$, respectively (Table S1). That is, the pre-treatment has only tiny influence on the Mn oxidation state.

Raman spectroscopy has the function of identifying phase and providing structural information [33]. As given in Fig. 1(c), under the electrochemical pre-treatment in Na_2SO_4 electrolyte, although the morphology of $\text{Mn}_3\text{O}_4\text{-A}$ maintained a cuboid structure and the surface was no longer flat. Some flocculent or void structure was observed. These structures greatly increased the contact between the electrolyte and electrode and promoted ion diffusion, which

was beneficial to improve the electrochemical properties [34–37]. As given in Fig. 1(c), all the Raman peaks were well indexed to the characteristic Raman peaks of Mn_3O_4 and carbon fiber paper, respectively. Among them, the sharp peak observed at 659 cm^{-1} was the most notable peak of hausmannite which corresponds to the Mn-O breathing vibration of divalent manganese ion in tetrahedral coordination [38,39]. Obviously, the peaks of $\text{Mn}_3\text{O}_4\text{-A}$ were more broadened than those of $\text{Mn}_3\text{O}_4\text{-I}$, indicating that a more disordered structure occurred after the electrochemical cycles [40]. It suggests that electrochemical reaction in Na_2SO_4 electrolyte reduces the crystallinity of $\text{Mn}_3\text{O}_4\text{-I}$.

As mentioned above, the electrochemical process did not modify the phase and valence of the electrode material, but only reduced the crystallinity of Mn_3O_4 . In order to further clarify the influence of the electrochemical process on the morphology and crystal structure. With SEM analysis, the initial morphology of the synthesized $\text{Mn}_3\text{O}_4\text{-I}$ appears as a regular prism with a smooth surface (Fig. 1d). After the Na^+ pre-treatment, the surface of the nanoparticles was no longer flat gradually although it remained basically prismatic. The particle size distribution by counting the length of 100 nanoparticles in the SEM image under the same magnification, exhibited the effect of the electrochemical pre-treatment on the morphology of Mn_3O_4 nanoparticles, as embedded in Fig. 1(d–f). In the electrochemical processes, the average length of the nanoparticles gradually decreased, from the

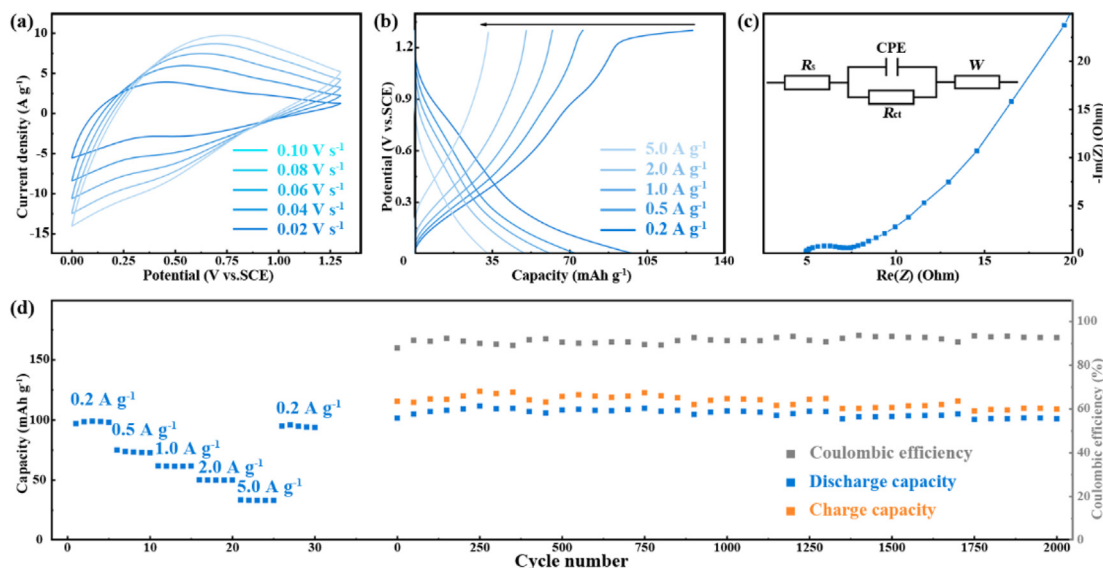


Fig. 2. Electrochemical performance of $\text{Mn}_3\text{O}_4\text{-A}$. (a) CV curves at different scan rates, (b) GCD profiles at different current densities, (c) Nyquist plot of $\text{Mn}_3\text{O}_4\text{-A}$ in MgSO_4 electrolyte, (d) the rate performance at different current densities and the cyclic stability and Coulombic efficiency at 0.2 A g^{-1} .

initial $\sim 143 \text{ nm}$ to $\sim 125 \text{ nm}$ (100th cycle) and to $\sim 115 \text{ nm}$ (200th cycle, $\text{Mn}_3\text{O}_4\text{-A}$). It indicated that the size of the nanoparticles gradually decreases and the surface gradually becomes rough. SEM image and EDS analysis (Fig. S2) show the chemical composition and distribution of $\text{Mn}_3\text{O}_4\text{-A}$. The elemental content of Na, Mn and O are 5.0%, 31.5% and 63.4%, respectively. The lower Na content and higher O content are possibly attributed to the adhesion of Na_2SO_4 in the electrolyte to the electrode surface, indicating that the Na^+ content in $\text{Mn}_3\text{O}_4\text{-A}$ was extremely low and can be ignored.

In Fig. 1(g–j), HRTEM images and IFFT show the atomic-scale features of $\text{Mn}_3\text{O}_4\text{-I}$ and $\text{Mn}_3\text{O}_4\text{-A}$. The (103) planes ($\sim 0.277 \text{ nm}$) of Mn_3O_4 can be observed for both $\text{Mn}_3\text{O}_4\text{-I}$ and $\text{Mn}_3\text{O}_4\text{-A}$, which corresponded to XRD patterns in Fig. 1(a). The well-defined lattice plane demonstrated that a good crystallinity of $\text{Mn}_3\text{O}_4\text{-I}$. After the pre-treatment, the amorphous structure and the tiny grains embedded in the amorphous structure in $\text{Mn}_3\text{O}_4\text{-A}$ were identified from Fig. 1(h). As the electrochemical activation was conducted, the amorphous feature gradually appeared and was stabilized after 200 cycles. *Ex-situ* Nyquist plots (Fig. S3) and discharge specific capacities (Fig. S4) were used to identify the electrochemical performance during the structural transformation. The specific capacity increased gradually and reached $\sim 100 \text{ mAh g}^{-1}$ in 1 M MgSO_4 solution after 200 cycles. It indicates that grain refinement exposed more active sites, further demonstrated in electrochemical mechanism characterization. With the electrochemical activation proceeding, the semicircles in the high frequency gradually decreased, suggesting the charge transfer resistance (R_{ct}) was reduced. The slope in the low frequency gradually increased, suggesting the ion diffusion resistance became smaller. Both the R_s and R_{ct} changed with cycle number, as shown in Table S2. Interestingly, there was a small decrease in R_s in EIS after 200 cycles. Therefore, we characterized the wettability of $\text{Mn}_3\text{O}_4\text{-I}$ and $\text{Mn}_3\text{O}_4\text{-A}$ (see Fig. S5). The measured contact angles of $\text{Mn}_3\text{O}_4\text{-I}$ (136.9°) and $\text{Mn}_3\text{O}_4\text{-A}$ (85.1°), demonstrate that the pre-treatment can reduce the resistance between electrode and electrolyte, which decreased the internal resistance (R_s) in three-electrode system. Combined with Fig. 1(j), the formation of the amorphous structure promotes the ion diffusion kinetics of Mn_3O_4 cathode. The different polarization between $\text{Mn}_3\text{O}_4\text{-I}$ and $\text{Mn}_3\text{O}_4\text{-A}$ can further explain the advantage of the unique amorphous-crystal composite, as shown in Fig. S6, which account also for the production of amorphous ion channels enhanced the

ion diffusion kinetics. As shown in Fig. S7, no obvious diffraction halos were observed, indicating that the amorphous structure was not the majority. For the formation mechanism of the amorphous structure, Mn^{2+} will dissolve from spinel Mn_3O_4 at the beginning of pretreatment, which leaves the chemical composition of the spinel Mn_2O_4 framework. The water molecules and Na^+ then intercalate into the tetrahedral (8a) space in the Mn_3O_4 framework [31,41]. The insertion of Na^+ restrains the spinel-to-layered transformation, as of no thermodynamic driving force for such occurrence [25]. In the subsequent pretreatment process, after Na^+ extracted from spinel Mn_2O_4 framework, the presence of water molecules and Mn^{2+} produced the amorphous ion channels, leading to the enhanced ion diffusion kinetics [40,42–46].

Through the characterization of electrode materials, it demonstrated that the Na^+ ion pre-treated spinel Mn_3O_4 can induce the occurrence of both amorphous phase and grain refinement. The formation of small-size grains greatly shortened ion transport path and increased the contact between the active sites and the electrolyte. It will be further analysed and proved in the subsequent electrochemical characterization and energy storage mechanism characterization.

3.2. Electrochemical characterization of $\text{Mn}_3\text{O}_4\text{-A}$

The electrochemical performance of the $\text{Mn}_3\text{O}_4\text{-A}$ for Mg^{2+} storage was tested through a three-electrode system. As shown in Fig. S8, the substrate (carbon fiber paper) had a low capacity indicating there is no capacity contribution from the substrate.

As shown in Fig. 2(a), the CV curves of $\text{Mn}_3\text{O}_4\text{-A}$ electrode had no obvious redox peaks, indicative of a pseudocapacitance reaction [43,47,48]. In the GCD curves (Fig. 2b), no obvious (dis)charging platforms were observed, consistent with the CV curves. The specific discharge capacitances of $\text{Mn}_3\text{O}_4\text{-A}$ were 98.9, 73.8, 61.5, 50.0, 33.1 mAh g^{-1} at current densities of 0.2, 0.5, 1.0, 2.0 and 5.0 A g^{-1} , respectively. The Nyquist plots of $\text{Mn}_3\text{O}_4\text{-I}$ and $\text{Mn}_3\text{O}_4\text{-A}$ were shown in Fig. S9 and Fig. 2(c), respectively. In the Nyquist plot, there are three components, including R_s (bulk resistance, the intersection of the semicircle curve at the real part Z' in the high frequency), R_{ct} (Faradic charge transfer resistance, the semicircle at the high frequency) and W (Warburg impedance, the slope of the curves at the low frequency) [49]. The $\text{Mn}_3\text{O}_4\text{-A}$ cathode showed smaller intersection of semicircle in contrast to $\text{Mn}_3\text{O}_4\text{-I}$

in the high frequency, exhibited a smaller R_{ct} , suggesting a smaller charge transfer resistance. In the low frequency, Mn_3O_4 -A showed a larger slope as compared to Mn_3O_4 -I, indicating a faster ion diffusion. The rate performance for Mg^{2+} storage was presented in Fig. 2 (d). The capacity can reach 98.9 mAh g^{-1} at a current density of 0.2 A g^{-1} and it can reach 33.2 mAh g^{-1} at a current density of 5 A g^{-1} . It is noteworthy that Mn_3O_4 -A demonstrated a superior rate performance: the capacity maintained at 95.8 mAh g^{-1} when the current density was returned to 0.2 A g^{-1} . The cycling stability test at a current density of 0.2 A g^{-1} was present in Fig. 2(d), i.e., a superior capacity retention rate of 99.4%. It suggests that Mn_3O_4 -A has relatively high specific capacity and considerable cycle stability. In Mg^{2+} storage process, our Mn_3O_4 -A has higher stability than phase conversion reaction. Comparison of discharge specific capacity and capacity retention of Mn_3O_4 -A and other ARMBs cathode materials was shown in Table S3. In contrast with the insertion/extraction reaction, Mn_3O_4 -A has a faster ion transformation rate and lower Coulomb interaction between Mg^{2+} and cathode due to amorphous ion diffusion channel and water molecules. In order to further illustrate the impact of pre-treatment ion species on amorphous ion channels, and then on electrochemical performance, the difference between the structure and electrochemical performance of Mn_3O_4 -A and Mn_3O_4 -Mg (pre-treated by Mg^{2+}) was compared, as shown in Fig. S10. It further proves that ion diffusion channels enable improving the electrochemical performance. Therefore, it has better cycle stability and capacity retention [16,20,50–52]. In order to further clarify the reaction mechanism of Mn_3O_4 -A for Mg^{2+} storage, the subsequent electrochemical mechanism characterization was carried out.

3.3. Electrochemical storage mechanism of Mn_3O_4 -A electrode

To interpret the electrochemical storage mechanism, especially the high-rate capability and high-capacity retention, the electrochemical kinetics of Mn_3O_4 -A electrode was investigated by a series of CV measurements at the scan rates from 0.5 to 3 mV s^{-1} .

Their peak currents (i) and scan rates (v) have a relationship as below:

$$i = av^b$$

where b represents the slope of $\log(i)$ vs. $\log(v)$ curve, often in a range of 0.5 – 1 . When b value is 0.5 , the electrochemical process is controlled by ion diffusion, corresponding to an insertion/extraction reaction. If b approaches 1 , the capacitor-like behavior would dominate the (dis)charging process.

The calculated b value (Fig. 3a) is 0.75 , indicating that both capacitive- and diffusion-controlled processes dominated the reaction of Mn_3O_4 -A cathode. The ratio of Mg^{2+} capacitive and diffusion contribution at a certain scan rate can be quantified by separating the current response i at a fixed potential v into capacitive- and diffusion-controlled charges, according to the Equation:

$$i(v) = k_1 v + k_2 v^{1/2}$$

where, k_1 and k_2 are constants at a given voltage [53]. As shown in Fig. 3(b), a dominant diffusion contribution of 34.6% can be quantified (light green region) in the CV curve at 2 mV s^{-1} . As the scan rate increased, the contribution from the capacitive process further increased to a maximum value of 70.2% at 3 mV s^{-1} (Fig. 3c). The nonnegligible diffusion-controlled contribution was achieved via Mg^{2+} inserted into amorphous structure, to be further explained in the subsequent XRD and XPS characterization. The dominating capacitive-controlled contribution will optimize the rate performance and the cycling stability of the Mn_3O_4 -A electrodes.

Furthermore, *ex-situ* XRD and *ex-situ* XPS measurements were carried out to explore the structural and valence state evolution of the Mn_3O_4 -A electrode at different potentials during the (dis)charging process. As shown in *ex-situ* XRD (Fig. 4a), during the entire (dis)charging processes, the characteristic diffraction peaks corresponded to (112), (211) and (003) of tetragonal hausmannite Mn_3O_4 (JCPDS No. 24–0734). No any shifts of peaks and change of

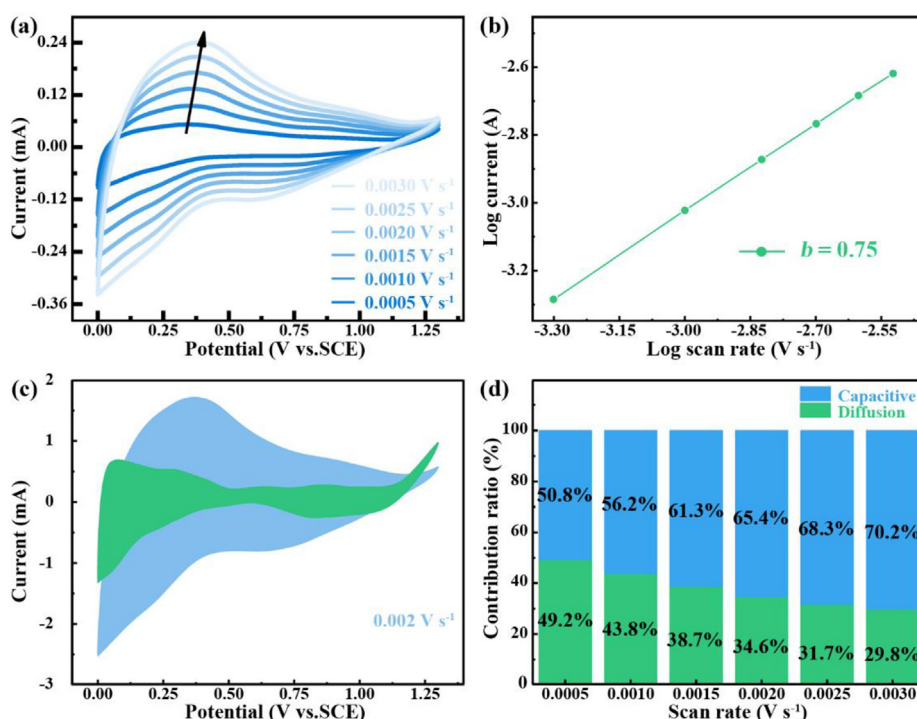


Fig. 3. Electrochemical kinetics of Mn_3O_4 -A cathode material in 1 M MgSO_4 aqueous electrolyte. (a) The CV curves at the range from 0.5 mV s^{-1} to 3 mV s^{-1} , (b) $\log i$ vs. $\log v$ plots at the highest current points in the process of charging, (c) CV curve with diffusion-controlled contribution at 2 mV s^{-1} , (d) bar chart showing the contribution ratio of capacitive- and diffusion-controlled capacities at different scan rates.

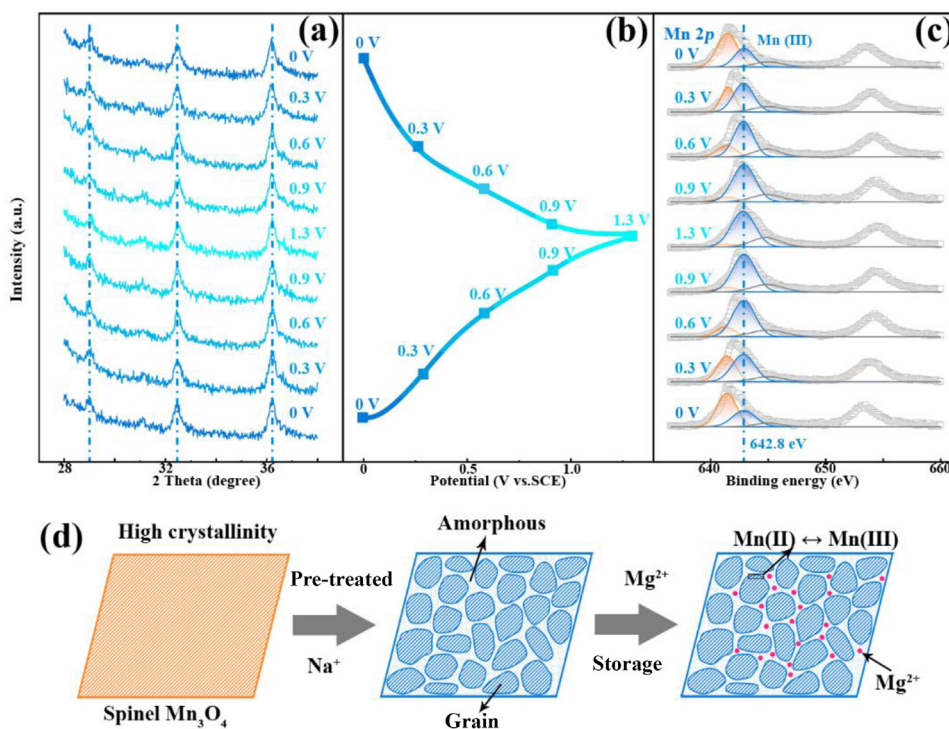


Fig. 4. Electrochemical storage mechanism of Mn₃O₄-A cathode material in 1 M MgSO₄ aqueous electrolyte. *Ex-situ* XRD (a) and the *ex-situ* XPS (c) during the (dis)charging (b) of Mn₃O₄-A cathode at a current density of 0.5 A g⁻¹. (d) Schematic illustration of the pre-treated by Na⁺ process and Mg²⁺ ion storage process of the spinel Mn₃O₄.

peak intensity were found, suggested that the spinel structure maintained during the insertion/extraction of Mg²⁺.

As shown in *ex-situ* Mn 2p XPS (Fig. 4c), the fitted peak area ratio of Mn (III) increased along with the charging process, and the ratios were 30%, 44%, 64%, 72% and 73% at 0, 0.3, 0.6, 0.9, and 1.3 V, respectively. Whereas, the fitted peaks area ratios of Mn (II) decreased from 52% (0 V) to 7% (1.3 V), and the proportion of Mn (IV) fitted peak area always remained ~ 20%. It indicated the oxidation reaction lied from Mn (II) to Mn (III), and there was no subsequent oxidation reaction from Mn (III) to Mn (IV) during the charging process. During the discharge process, the proportion of the fitted peak area of Mn (II) gradually increased from 5% to 55%, and the proportion of the fitted peak area of Mn (III) gradually decreased from 73% to 27% as the electrode potential decreases. It indicated that the reduction reaction also conformed to the change from Mn (III) to Mn (II). As a result, it achieved a highly reversible charge and discharge reactions in Mg²⁺ electrochemical storage process. In total, the ratios of Mn (II), Mn (III) and Mn (IV) were returned to initial ration, indicating the high reversibility of Mn₃O₄-A, as shown in Table S4. Combined with the *ex-situ* XRD patterns, the (sub-)surface of Mn₃O₄-A undergoes the transformation between Mn (III) and Mn (II) during (dis)charging processes.

From the electrochemical kinetics and the *ex-situ* XRD and XPS, the electrochemical storage mechanism has been exclusively explained, as shown in Fig. 4(d). It is noted that the capacitive contribution of Mn₃O₄-A occupies a higher contribution ratio. This can account for the high rate performance. The electrochemical reaction process of Mn₃O₄-A was revealed: Mg²⁺ ions insert and extract in the amorphous ion diffusion channels and there is a (sub-) surface pseudocapacitance reaction between Mn (II)/(III) during (dis)charging processes without any phase transformation. Since the overall structure has not been destroyed, which is also the reason why Mn₃O₄-A has excellent cycle life and capacity retention.

4. Conclusion

In summary, the pre-treated spinel Mn₃O₄ exhibited faster Mg²⁺ diffusion kinetics and more exposed active sites, respectively, which achieved high specific discharge capacity of 98.9 mAh g⁻¹ and excellent capacity retention rate of 99.4%. The pre-treated in Na₂SO₄ solution induces the amorphous structure, in favor of Mg²⁺ diffusion, and grain refinement, conducive to both Mg²⁺ and electron transportation. To the best of our knowledge, this is the first time to achieve the Mg²⁺ storage via a spinel Mn₃O₄, and we clarified the reaction mechanism through a suite of *ex-situ* characterization. The storage mechanism of Mn₃O₄ cathode in Mg-ion batteries is the (sub-)surface pseudocapacitance reaction through Mn (II) and Mn (III), which achieved high capacity and structural stability. Thus, our research not only provides a new storage mechanism for spinel Mn₃O₄ in aqueous batteries, but also enables a high cycle stability electrode material for rechargeable aqueous Mg²⁺ storage.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jechem.2021.11.031>.

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