Investigation into the origin of high stability of δ -MnO₂ pseudo-capacitive electrode using operando Raman spectroscopy

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ABSTRACT

Manganese oxides of different structures, especially α -MnO₂, have been extensively studied as electrodes for pseudocapacitors. However, the poor stability associated with intercalation of proton has been the main obstacle to their commercial applications. To effectively mitigate this problem, it is necessary to fully understand the energy storage mechanism of the MnO₂ phases. In this study, δ phase MnO₂ has been synthesized through controllable electroplating on architectural Ga-doped ZnO (GZO) bones, demonstrating a high specific capacitance of 1,068 F g⁻¹ and high stability (slight performance drop focus on the first 2,000 cycles and then remained relatively constant in the subsequent 13,000 cycles). The charge storage mechanism of the δ -MnO₂ coated GZO has been carefully investigated at this limiting reaction

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condition. Results suggest that the amount of charge stored in the electrode material correlates well with the amount of Na^+ inserted into the electrode material from the electrolyte. It is also noted that no spectral features corresponding to H^+ insertion were detected during cycling when the sample was probed using *in operando* Raman spectroscopy. **Therefore, for layered $\delta\text{-MnO}_2$, a charge storage mechanism of Na^+ intercalation/deintercalation dominated, accompanied by interlayer spacing expansion/contraction, is proposed.** Moreover, theoretical calculations also confirmed that the insertion of Na^+ is more energetically favorable than H^+ at all sites of the interlayer in $\delta\text{-MnO}_2$, offering a rational explanation of the proposed mechanism and the observed excellent stability.

Key words: $\delta\text{-MnO}_2$, pseudo-capacitor, charge storage mechanism, *in situ* Raman spectroscopy, DFT calculation.

1. Introduction

Supercapacitors (SCs), also called ultracapacitors, are ideally suited for bridging the gap in performance between batteries and conventional capacitors [1,2]. They are playing an increasingly important role in energy storage and conversion for many applications. Moreover, the popularity of supercapacitors in the electric vehicle power supply market is also fast growing because of their outstanding performance characteristics such as high power density and long cycle stability [3,4]. However, many emerging markets demand higher energy density and lower cost. In recent

decades, electrode materials of high theoretical capacity have attracted much attention, including transition metal oxides [5-7], hydroxides [8,9], carbides [10], and nitrides [11]. Because of the redox reactions or phase changes associated with these transition metal compounds, they display much higher energy densities, almost one order of magnitude higher than those of the carbon based electric double layer capacitors (EDLC).

In addition to the widely known pseudocapacitive electrode materials, RuO_x and MnO_2 , a large numbers of other transition metal compounds are recently reported one after another. However, most of these electrode materials exhibit a pair of redox peaks in a typical cyclic voltammetry (CV) or a voltage plateaus during galvanostatic cycling and only “extrinsic” pseudocapacitive performance emerged, although they do display large capacitance when tailored into nanoscales [12]. It seems that RuO_x and MnO_2 are two of the few materials that display ideal pseudocapacitive behaviour: near square-shape CV and linear current-voltage relationship during galvanostatic cycling. As is well known, RuO_x is expensive and harmful to the environment (only work in high density acid electrolyte). Thus, MnO_2 is a more promising material for SCs because of its natural abundance, low cost, low toxicity, high theoretical specific capacitance ($1,380 \text{ F g}^{-1}$ and $1,109 \text{ F g}^{-1}$ in a potential window of 0.8 V and 1 V, respectively), and wide potential window [7]. MnO_2 -based electrodes have been extensively studied in recent years. To date, however, the commercialization of MnO_2 based electrodes is still hindered largely by their poor conductivity and inadequate cycling stability [13,14]. The poor conductivity of MnO_2 can be mitigated by

incorporating highly conductive phases [15,16] or doping with proper elements [17,18]. However, the poor cycling stability is a much hard problem to address; it is associated with electrochemical dissolution induced by the disproportionation reaction originated from the involvement of proton [19], as well as crystal structure change induced by Jahn-Teller effect [20]. A profound understanding of the charge storage mechanisms in different phases of MnO₂ is necessary to overcome this challenge.

For the pseudocapacitive behaviors of MnO₂, the widely accepted Faradic reactions associated with energy storage/release processes include intercalation/deintercalation of protons (H⁺) and metal cations (M⁺) in electrolyte [2,21] as expressed below:

The H⁺ involved process has been confirmed through XPS and Raman measurements under certain conditions since it was proposed [21,22]. Unfortunately, intermediate phase MnOOH is unstable and can be easily transformed to MnO₂ and soluble Mn²⁺, which can result in dissolution of MnO₂ active materials and hence fast degradation in electrochemical performance. However, it is still unclear whether there is a way to avoid this dissolution and how the rates of these reactions depend on the phases or crystal structures of MnO₂. We believed that it is easier to mitigate this problem of MnO₂ based electrodes than to develop new electrode materials for commercially viable pseudo-capacitors. Our recent investigation [22-24] into phase evolution of α -MnO₂ and Mn₃O₄ during charging and discharging processes using *in operando* Raman spectroscopy suggest that the electrochemical behaviors of the MnO₂ depend

sensitively on their phase structures, which has also been mentioned in Charles B. Musgrave's work [25]. Thus, it is possible to identify a particular crystal structure of MnO_2 that may preclude the incorporation of proton during charging/discharging, thus dramatically enhance the long-term cycling stability of supercapacitors.

Reversible phase transformation of MnO_2 nanosheets from hexagonal to monoclinic structure has ever been studied via an *in situ* Raman technique by Chen's group, which is responding to the intercalation/deintercalation of Na^+ between nanosheets [26]. However, very limited investigations were performed and no definite energy storage mechanism and its relation with electrochemical performance was proposed. Here, we report our findings in synthesis of highly porous layered $\delta\text{-MnO}_2$ with good conductivity for pseudo-capacitive electrodes, demonstrating initial specific capacitance of $1,068 \text{ F g}^{-1}$, very close to the theory value, in a potential window of 0~0.9 V (vs: Ag/AgCl) and unprecedented stability in 1 M Na_2SO_4 aqueous solution. Though the Ga doped ZnO nano wires (GZO NWs) backbone experienced a mechanical failure at the first 2,000 galvanostatic charge/discharge (IV) cycles, the remained $\delta\text{-MnO}_2$ exhibited a very high cycling stability in the subsequent 13,000 cycles. The initial morphology of the $\delta\text{-MnO}_2$ active materials is nano particles, which transformed into thin flakes after chemical activation. The charge storage mechanism of the $\delta\text{-MnO}_2$ was revealed using energy-dispersive X-ray spectroscopy (EDX) and *in-situ* Raman spectroscopy. Results suggest that the amount of charge stored in the electrode material correlates well with the amount of cations inserted into the electrode material from the electrolyte, e.g. the Na/Mn ratio is about 1:2 when

the obtained capacitance was about 580 F g⁻¹. Furthermore, no signals from H⁺ were observed when the sample was measured with *in operando* Raman during the charge/discharge process at very low sweep rate. These results implied that only electrolyte cation, Na⁺, was involved in the energy storage process. Thus, the energy storage behavior is dominated by an interlayer spacing contraction/expansion due to Na⁺ intercalation/deintercalation without the involvement of proton. Moreover, adsorption energies (E_{ads}) of Na⁺ and H⁺ were also computed to explain why electrolyte cations but not smaller protons prefer inserting into the interlayer of δ -MnO₂.

With a profound understanding of the energy storage/release mechanism of δ -MnO₂, it is reasonable to believe that well designed δ -MnO₂ may display high capacity and adequate cycling stability, which will be the most attractive pseudo-capacitive material for commercial applications. In this study, we start with the most promising transition metal oxide (MnO₂), taking advantage of a well-designed electrode architecture, to create a unique electrode having specific capacitance close to the theoretic value. We have carefully synthesized and systematically investigated into the pseudocapacitive behaviour and energy storage mechanism of the active material δ -MnO₂ under the conditions to ensure almost all active material was involved in the Faradic reaction, in an effort to explore the fundamental limit of storage capacity. The reported δ phase MnO₂-based electrode materials are believed to be the most promising electrode for high-performance supercapacitors for many emerging applications.

2. Experimental procedure

2.1 Sample synthesis

All reagents were analytical grade and used without further purification. GZO NWs were synthesized by a simple hydrothermal reaction, followed by heat treatment under 8% H₂-N₂ flow. Briefly, carbon fiber paper (CFP) (Hesen, Shanghai Electric. Co.) was soaked in 0.5 M KMnO₄ for 30 min, cleaned with deionized water, and dried in an oven for 30 min at 60 °C. In a typical experiment, 65 ml precursor solution was prepared with 0.2842 g zinc nitrate hexahydrate and 0.1346 g of hexamethylenetetramine (HMTA), added with 0.5% gallium nitrate (molar ratio to zinc nitrate) under constant magnetic stirring for 30 min, and then added with 3 ml ammonia during the magnetic stirring. Then the pre-treated CFP was dipped into the precursor solution, sealed in a bomb with a volume of 82 ml and kept in an oven at 90 °C for 24 h. CFP coated with white products was then obtained and washed with DI water, named as Ga doped ZnO supported CFP substrates, denoted as GZO/CFP for short. Second, the as-obtained substrates were further thermally annealed in 8% H₂-N₂ atmosphere at 450 °C for 2 h. ZnO NWs samples (ZnO/CFP) without Ga doping or annealing were also prepared for comparison. Finally, manganese oxide film was electrodeposited on the substrates in a solution containing 0.1 M Mn(CH₃COO)₂ and 0.1 M Na₂SO₄ using a three-electrode configuration CHI 660E (Chenhua, Shanghai, China) with a Ag/AgCl reference electrode and a platinum counter electrode, which was performed by a two-step process with alternative potentials of 0.40 V for 20 s and 0.45 V for 60 s (versus Ag/AgCl). Then the as-obtained sample was washed with DI

water and kept in an oven at 140 °C for 4 h and was recorded as GZO@MnO₂. The mass of the electroplated MnO₂ was calculated by integrating the total Coulombic charges used for deposition.

2.2 Characterization

The microscopic features of the electrode materials were characterized by a field emission scanning electron microscope (FE-SEM, Hitachi LEO 1530) equipped with an energy-dispersive X-ray spectroscopy (EDX) detector and a field emission high resolution transmission electron microscope (HRTEM, JEOL JEM-2100F). The chemical state of the electroplated MnO₂ was analyzed by X-ray photoelectron spectroscopy (XPS, PHI X-tool) with Al K α (mono) anode at energy of 51 W in a vacuum of 10⁻⁷ Pa. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer with Cu K alpha radiation ($\lambda = 0.15406$ nm) at a nearly parallel grazing incidence angle of 3 degrees. In situ Raman spectra were acquired using a LabRAM HR Evolution system equipped with deep-depleted thermoelectrically cooled CCD array detector, an Ar laser (wavelength $\lambda = 514.5$ nm) and a long working distance of 50 $\times$ objective lens. Raman spectra of the sample were captured one by one via a mapping mode (one spectrum per 100 seconds) while a cyclic voltammetry test in a three-compartment cell was run at a sweep rate of 1 mV s⁻¹. Raman signal change (corresponding to band change of the sample) was only detected during the charging and discharging process to explore the energy storage-release behavior of the active material. The exploration time applied was 14 seconds with two sweeps per spectrum, and the size of the optical hole used was 100

mm.

2.3 Electrochemical test

The electrochemical properties of electrode sample were studied using a CHI 660E workstation in a three-electrode configuration with the samples as working electrode, and Ag/AgCl (in saturated KCl) and a Pt mesh as reference and counter electrode, respectively. A solution containing 1 M Na₂SO₄ served as the electrolyte at room temperature. Galvanostatic charge-discharge durability tests were performed between 0 and 1 V vs. Ag/AgCl at a current density of 60 A g⁻¹.

3. Results and discussion

Free-standing CFP supported sample were prepared by a two-step process, the synthesis of GZO NWs on CFP through a hydrothermal process and the subsequent electroplating of MnO₂ on the GZO NWs (**Figure 1a**). In order to ensure high electrical conductivity of GZO NWs (which will be the current collector for the plated MnO₂), Ga/Zn molar ratio in the precursor solution was tuned to be 0.5% to allow proper amount of Ga doped into the ZnO NWs; the ratio was confirmed by EDX analysis (**Figure S1**). This preparation method is similar to the one reported by Enrico and co-workers [27] with some modification to tailor the conductivity. Scanning electron microscopy (SEM) studies show that the obtained GZO NWs have an average diameter of 170 nm and length up to around 7 μm (**Figure 1b**). After the electroplating of MnO₂, which presented a morphology of nano particles and uniformly coated on the surface of GZO NWs (**Figure 1c**), the diameters of GZO NWs were slightly reduced after the deposition of MnO₂, implying partly dissolution

of GZO during the anodic electroplating process. After 2,000 galvanostatic charge-discharge cycles at 60 A g^{-1} in 1 M Na_2SO_4 aqueous solution, only a highly porous thin film coating was left (**Figure 1d**), which is composed of very thin flakes with a thickness of several nano meters (**Figure 1e**). Despite mechanical failure of the GZO supporter, large random holes were left upon cycling, which should be beneficial to the fast transport of electrolyte ions.

To uncover the crystal texture of MnO_2 nanoparticles on the GZO surface, we used Raman spectroscopy together with X-ray photoelectron spectroscopy (XPS). Phase change of the active electrode materials in a 1 M Na_2SO_4 electrolyte solution before and after cycling was revealed using Raman spectroscopy (**Figure 2a**). While the distinct bands at 98, 334, 438, and 538 cm^{-1} are assigned to ZnO [28], the broad bands at 612 and 634 cm^{-1} can be attributed to MnO_2 , corresponding to the Mn-O vibration along the chains of the MnO_2 framework and the symmetric stretching vibration of Mn-O bond in the $[\text{MnO}_6]$ octahedra, respectively [29]. The width of the broad bands is an indication of poor crystallinity of the plated MnO_2 nanoparticles. After 15,000 cycles of charge and discharge, the Raman signatures of the ZnO phase disappeared but several distinctly different bands emerged at 645, 579, 492, 413, and 286 cm^{-1} , which are similar to the Raman spectrum for a sample cycled for 2,000 times (**Figure S2**) except that the bands are more distinctly separated. All these bands can be assigned to layered $\delta\text{-MnO}_2$ composed of octahedra $[\text{MnO}_6]$ sharing edges [30]. The evolution of the Raman spectra suggests that the active material was transformed to layered $\delta\text{-MnO}_2$ with better crystallinity from an amorphous structure during cycling,

which is in good agreement with the XRD results of a thick MnO₂ electrode (**Figure S3**).

The surface chemistry of the as-prepared sample was further investigated using XPS (**Figure 2b**). Characteristic peaks corresponding to Mn, Zn, O and C are apparent in the overview profile (**Figure S4**). The two peaks at the binding energies of 641.9 eV and 653.5 eV in the XPS spectrum (**Figure 2b**), with a spin-energy separation of 11.6 eV, can be assigned to the Mn 2p_{3/2} and 2p_{1/2} orbits of Mn⁴⁺, respectively [31,32]. The Mn 3s spectrum (**Figure 2c**) displays doublet peaks which are derived from the parallel spin coupling between the electrons in 3s and 3d orbitals, with a splitting width of ~ 4.7 eV, indicating that the Mn cations in this oxides have an average valence close to 4 [33,34]. The XPS spectrum of O 1s (**Figure 2d**) can also be used to estimate the valence of Mn cations, and this spectra can be deconvoluted into two components, including 85% oxide (O-Mn-O) and 15% hydroxide (Mn-O-H) calculated from the peak area, which is in agreement with previous data observed in MnO₂ [35].

High-resolution transmission electron microscopy (HRTEM) was used to reveal the details of MnO₂ phase structure (**Figure 3**). It can be seen that the electroplated MnO₂ particles with a size of several nanometers are well coated on the surface of GZO skeleton (**Figure 3a**). Moreover, two lattice fringes in a very small particle are measured to be 0.270 nm and 0.232 nm (**Figure 3b**), corresponding to (011) and (20 $\bar{2}$) planes of δ -MnO₂, respectively. A schematic lattice of δ -MnO₂ (American Mineralogist 94:816-826) and ZnO substrate (JCPDS 70-2551), rotated to the same

orientation of the observed structure shown in **Figure 3b**, is also presented here in **Figure 3c**. It is also noticed that the 0.270 nm lattice fringe of δ -MnO₂ is very close to that of the ZnO substrate (**Figure 3b and c**), which greatly influence the orientation of the MnO₂ deposition. Since the diameters of the GZO NWs are reduced slightly after the anodic deposition of MnO₂, some dissolution of Zn ions may take place during MnO₂ deposition. Thus, it is reasonable to propose the following processes for the deposition of MnO₂ on GZO:

The Mn⁴⁺ and the oxygen ions then rearranged into a new MnO₂ structure. After long term cycling, GZO NWs disappeared and only very thin flakes were left (**Figure 3d**), which is in agreement with our microscopic analysis (**Figure 1d**). The HR-TEM image shows a lattice fringe of 0.239 nm, corresponding to the (20 $\bar{2}$) plane of δ -MnO₂ (**Figure 3e**), suggesting that the δ -MnO₂ nanoparticles were transformed to very thin nanoflakes of large dimension as the GZO NWs were dissolved during the cycling. The TEM analyses are in good agreement with the SEM and Raman investigation discussed earlier, clearly indicating that the active material MnO₂ experienced a dissolution and then recrystallization process during the early stage of electrochemical cycling.

Figure 4a shows the cyclic voltammograms (CVs) of different electrodes acquired at a voltage scan rate of 50 mV s⁻¹: pure GZO NWs, as-prepared MnO₂

deposited on CFP, ZnO@MnO₂, and GZO@MnO₂ on CFP. The much larger CV area of the GZO@MnO₂ electrode indicates much higher areal specific capacitance than those of ZnO@MnO₂ and MnO₂ electrodes. It is noted that the contribution to capacitance of the GZO NWs and the CFP is negligible since their corresponding CV area is relatively small. The superior capacitance performance of GZO@MnO₂ electrode is attributed to the enhanced electrical conductivity and rapid ions transport path of the unique architecture of the GZO NWs backbone, which allows full utilization of all active MnO₂ for charge storage. The GZO@MnO₂ electrode (electrodeposited MnO₂ mass loading of 0.12 mg cm⁻²) exhibits nearly twice specific capacitance (976 F g⁻¹ at 2 mV s⁻¹) as that of the MnO₂ electrode electroplated directly on pure CFP (493 F g⁻¹) under similar conditions (**Figure S5**). These results suggest that GZO NWs play a vital rule in achieving the observed high capacity of MnO₂. Electrochemical impedance spectroscopy (EIS) was also used to investigate the electrochemical property of these electrodes. EIS analysis suggests that the GZO@MnO₂ electrode has the most favorable impedance response for charge storage among all samples tested (**Figure S6**). Further, the CVs of the GZO@MnO₂ electrode maintain symmetrically rectangular shapes in a wide range of scan rates (from 2 mV s⁻¹ to 200 mV s⁻¹), suggesting an excellent rate capability and less resistive behavior (**Figure 4b**). The effect of active electrode material mass loading on electrochemical performance is also investigated, as shown in **Figure S7**.

According to a previous study, the surface-controlled capacitive effect and the diffusion-controlled insertion can be distinguished from the dependence of the current

(i) on the potential scan rate (v) using the following equation [36,37]:

$$i = a v^b$$

Where a and b are adjustable parameters. **Figure 4c** shows a plot of $\log(i)$ versus $\log(v)$ for scan rates varied from 2 to 200 mV s^{-1} . Both the anodic and cathodic currents were acquired at 0.4 V. Since the slope of the plots, b values, are very close to 1 (**Figure 4c**), the current is predominantly capacitive in nature. Thus, the charge storage of the electrode is due mostly to a surface redox-controlled process rather than a diffusion-controlled process, thus offering superior rate capacity (benefited from the nanostructures of the electrodes).

In order to gain deeper insight into the energy storage mechanism of the $\delta\text{-MnO}_2$, *in operando* Raman spectroscopy was used to directly probe the evolution in structural features of the $\delta\text{-MnO}_2$ electrode material during charge/discharge cycling (**Figure 5b**). For this *in operando* investigation, a unique three-compartment electrochemical system [24] was developed and incorporated into our Raman microscope, allowing acquisition of Raman spectra of the $\delta\text{-MnO}_2$ electrode at different states of charge or discharge (or applied voltage) in the voltage range between 0 and 1.0 V (**Figure 5**). There are three major Raman regions, in which the bands shift as a function of the applied voltage, due mainly to structural transformation during charge/discharge: 674~680 (ν_1), 572~589 (ν_2), and 501~510 cm^{-1} (ν_3), as shown in Figure 5a. According to the preliminary assignments of Julien *et al* [30], the ν_2 band (572~589 cm^{-1}) and ν_3 band (501-510 cm^{-1}) are the typical Raman feature for layered manganese dioxides of the birnessite family, which can be assigned to the Mn-O stretching vibrations of

[MnO₆] octahedra. It should be noted that a band located at 600-650 cm⁻¹ was also observed with relatively weak intensity, which corresponds to the symmetric stretching mode of the [MnO₆] octahedra. The ν_2 Raman band (572~589 cm⁻¹) is attributed to the stretching vibration in the basal plane of the [MnO₆] slabs. With the applied potential was increased from 0 V to 1 V, the ν_2 (Mn-O) stretching mode underwent a red shift from 587 cm⁻¹ to 572 cm⁻¹ upon Na⁺ ion extraction and the accommodation of water from the solvent, which can be attributed to the change in the oxidation state of Mn ion and the weakening of the interaction between [MnO₆] slabs due to the expansion of interplanar spacing (**Figure 5c**). On the other hand, when the applied potential was decreased from 1 V to 0 V during discharge, the ν_2 band shifted back from 572 cm⁻¹ to 589 cm⁻¹ with the Na⁺ ions inserting into the interspace of the [MnO₆] slabs and the contraction of the interplanar spacing. Noticeably, when the applied potential was increased to 0.7 V during charge in the anodic direction, a new peak (ν_1 at about 677 cm⁻¹) that should be related to an intermediate oxide state of MnO₂ and stands for the coexistence of Mn⁺⁴ and Mn³⁺ [38] appeared and its intensity increased gradually with the applied potential till 1.0 V, an indication of oxidation of Mn²⁺ reserved in the δ -MnO₂ after the escape of Na⁺. There is also an intensity enhancement of all these three Raman bands (ν_1, ν_2, ν_3) along with the rising of potential and an opposite change with its declining. Most importantly, there is no observable Raman feature corresponding to the expected middle phase MnOOH resulting from the well accepted intercalation/deintercalation of H⁺ for the energy storage of MnO₂. This intermediate phase MnOOH is unstable and can easily

evolve into MnO_2 and soluble Mn^{2+} , which accounts for the active electrode materials loss and leads to major capacitance fading of the MnO_2 based electrode. This electrochemical dissolution during the cycling process has been well recognized in some investigations [39,40]. Our results have demonstrated that the inhibition of MnOOH disproportionation reaction and the inconspicuous structure change of $\delta\text{-MnO}_2$ during cycling is vital to achieving exceptional cyclic stability while maintaining high capacitance.

To further investigate why proton (H^+) may not be involved in energy storage by insertion into the interlayers of $\delta\text{-MnO}_2$ during cycling, we resorted to spin-polarized density functional theory (DFT) computations with a 3D periodic boundary condition at the GGA-PW91 level [41,42]. The kinetic cutoff energy for the plane wave basis was set at 600 eV with PAW method [43,44]. The Brillouin-Zone integration was sampled at 0.05×2 ($1/\text{\AA}$) interval in the reciprocal space by Monkhorst-Pack scheme [45]. The $\delta\text{-MnO}_2$ electrode was modelled using layers of tetragonal planes, very thin $\delta\text{-MnO}_2$ flakes, with a surface area of $10 \times 10 \text{ \AA}$ and interlayer separation of $7 \text{ \AA}$, as seen in Figure 6. Adsorption energies (E_{ads}) of Na^+/H^+ on $\delta\text{-MnO}_2$ at open circuit potential (OCP) were calculated with the following equation:

$$E_{\text{ads}} = E(\delta\text{-MnO}_2 - \text{M}^+ + \text{e}^-) - E(\delta\text{-MnO}_2) - E(\text{M}^+ + \text{e}^-)$$

where $E(\delta\text{-MnO}_2 - \text{M}^+ + \text{e}^-)$, $E(\delta\text{-MnO}_2)$, and $E(\text{M}^+ + \text{e}^-)$ correspond to the energies for Na^+/H^+ adsorbed on $\delta\text{-MnO}_2$, the clean $\delta\text{-MnO}_2$ and the unbonded Na^+/H^+ , respectively. All possible adsorption locations of H^+/Na^+ with $\delta\text{-MnO}_2$ are considered. The side/top views of their adsorptions structures are shown in **Figure 6** and the

related E_{ads} , adsorption configurations, and bond lengths are listed in **Table 1**. H^+ located in the middle of the interlayer (**H-middle**) shows negligible E_{ads} , indicating non-bonding, while strongly adsorbed on the top of O (**H-top**). Na^+ is also stable on those two sites (**Na-middle** and **Na-top**); nevertheless, Na^+ strongly adsorbed on both sites, attributable to its larger radius. Additionally, Na^+ has another two preferential adsorption sites, 3-fold-hollow site of three surface O with subsurface Mn and O in the hollow (**Na-3fh-Mn** and **Na-3fh-O**, respectively), which show even stronger E_{ads} . Thus, E_{ads} of Na^+ in $\delta\text{-MnO}_2$ are much stronger than that of H^+ for all possible sites, which means that Na^+ but not smaller protons prefers inserting into the interlayer of $\delta\text{-MnO}_2$. The energetic trends are unchanged in charge/discharge processes as applied voltages concurrently shift the energies of electrons for all adsorptions. The computation results are quite coincident with the EDX analysis and the *in operando* Raman results, further confirming the energy storage mechanism of layered $\delta\text{-MnO}_2$ discussed above.

Table 1. Adsorption energies (E_{ads}) at OCP for H^+ and Na^+ ions on $\delta\text{-MnO}_2$ (001) slabs with 7-Å interlayer.

	E_{ads} (ev)	Configuration	Bonding
H-middle	-0.01	In the middle of interlayer	No bonding
H-top	-3.15	On top of O	H-O = 0.98 Å
Na-middle	-3.83	In the middle of interlayer	Na-O = 2.87 Å
Na-top	-3.92	On top of O	Na-O = 2.27 Å
Na-3fh-Mn	-4.06	In 3-fold-hollow site of 3O with Mn in the hollow	3× Na-O = 2.44 Å
Na-3fh-O	-4.10	In 3-fold-hollow site of 3O with O in the hollow	3× Na-O = 2.41 Å

4. Conclusions

In conclusion, porous $\delta\text{-MnO}_2$ grown on Ga-doped ZnO as electrodes for pseudocapacitors have been synthesized and characterized firstly. Because of the

much improved electrical conductivity of GZO, the electrode exhibits an ultrahigh initial specific capacitance of 1,068 F g⁻¹ and a near-linear I-V relationship during galvanostatic cycling. Contrary to other reports about MnO₂ based electrodes, our δ -MnO₂-based electrodes exhibited high specific capacity as well as excellent cycling stability. The subsequent doping of Ga along with cycling seems to increase the electrical conductivity of the δ -MnO₂ by introducing more mobile charged defects in the lattice. Most importantly, *in operando* Raman spectroscopy was used to monitor the phase evolution of δ -MnO₂ during the charge/discharge cycling. It was found that, as the cell voltage was increased and decreased, the interlayer distance between the [MnO₆] slabs expanded and contracted, respectively, as inferred from the Raman band shift under *in operando* conditions. However, there were no Raman spectral features that suggest proton was involved in the energy-storage mechanism of layered δ -MnO₂, which was further confirmed by EDX analysis. This is also consistent with the fact that the amount of charge stored in the electrode material correlates well with the amount of Na⁺ inserted into the electrode, implying negligible contribution to capacitance of proton. Hence, a non-H⁺-involved energy storage process has been proposed for the δ phase MnO₂. Further, DFT calculations explained why Na⁺ has stronger E_{ads} and is more thermodynamically favorable than H⁺ at all interlayer sites of δ -MnO₂. Finally, our results also imply that not only the composition of electrode material but also the crystal structure and defect structure (affected by doping) may greatly influence the energy storage behavior of a specific electrode. We believe that the layered δ -MnO₂-based electrode materials have potential to achieve high power

and energy density as well as long cycle life for supercapacitors.

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Figure Captions

Figure 1. (a) Schematic illustration for the synthesis process of GZO@MnO₂ on CFP substrate.. SEM images of the electrode material: (b) GZO (Ga-doped ZnO) NWs grown on carbon fiber paper, (c) MnO₂ coated GZO (after electroplating of MnO₂ for 1 min), (d) after galvanostatic charge-discharge cycling of 2,000 times at a current density of 60 A g⁻¹ and (e) a closer view of the detailed features of the active electrode material, δ -MnO₂.

Figure 2 Crystal texture of the MnO₂ on the electrode. (a) Raman spectra of the electrode before (blue) and after (red) galvanostatic charge/discharge for 15,000 cycles. XPS spectra of (b) Mn 2p, (c) Mn 3s, and (d) O 1s for the as-prepared MnO₂ on GZO/CFP electrode.

Figure 3 HRTEM images of a Ga-doped ZnO nanowire coated with a MnO₂ nanoparticle (taken from an as-prepared sample). (a) a low magnification image, (b) a closer view of the area indicated by the red box in (a). The fringe spacing of 0.270 nm and 0.232 nm correspond to the separation between the (20 $\bar{2}$) and the (011) lattice planes of δ -MnO₂. (c) A schematic lattice of δ -MnO₂ and ZnO with purple, blue, red spheres standing for Mn, Zn, and O atoms, respectively. (d) TEM and (e) HRTEM images of the sample after long-term cycling. The fringe spacing of 0.239 nm corresponds to the separation between the (20 $\bar{2}$) lattice planes of δ -MnO₂.

Figure 4 Electrochemical performance of the electrodes. (a) CV curves at a sweep rate of 50 mV s⁻¹ of the electrodes (GZO, MnO₂, ZnO@MnO₂, and GZO@MnO₂) with MnO₂ plating time of 1 min on different substrates. (b) CV curves of the

GZO@MnO₂-1 min at different sweep rates. (c) Dependence of the anodic and cathodic currents at 0.4 V on the potential scan rate, v , using $i = av^b$ when v was varied from 2 to 200 mV s⁻¹. (d) Galvanostatic charge/discharge curves of the GZO@MnO₂-1 min collected at different current densities. (e) Dependence of specific capacitance on scan rate (lower axis) and on current density (upper axis) as determined from the CV curves and the galvanostatic charge/discharge curves, respectively. (f) Capacitance retention of the GZO@MnO₂ electrode with MnO₂ plating time of 1 min and 30 min (inset) as a function of cycle number. The capacitances were calculated from the discharge curves at a constant current density of 60 A g⁻¹ for GZO@MnO₂-1 min and 18 A g⁻¹ for GZO@MnO₂-30 min electrodes, respectively.

Figure 5. Electrochemical *in operando* Raman study of a cycled δ -MnO₂ electrode. (a) *In operando* Raman spectra acquired at different states of charge/discharge in 1 M Na₂SO₄. (b) The corresponding charge/discharge CV curve at a scan rate of 1 mV s⁻¹. (c) Schematic diagram of the interplanar spacing change of the layered δ -MnO₂ during the charge/discharge process according to the Raman analysis.

Figure 6. Schematic diagram of δ -MnO₂ during cycling. (a) the model δ -MnO₂ of tetragonal planes with a 7-Å interlayer and (b) the related adsorption structures listed in Table 1. The purple, red, green, and blue spheres stand for Mn, O, H, and Na atoms, respectively.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Recent personal portrait photo and a biosketch of authors

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Graphical abstract

MnO₂ coated Ga-doped ZnO electrodes demonstrate a specific capacitance of 1,068 F g⁻¹ and unprecedented stability in Na₂SO₄, the charge storage mechanism of which was dominated by an interlayer spacing contraction/expansion due to Na⁺ intercalation/deintercalation without the involvement of proton, which was illuminated by a joint experimental and theoretical study.