Electrochemical Synthesis and Supercapacitive Properties of \( \varepsilon \)-MnO\(_2\) with Porous/Nanoflake Hierarchical Architectures

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A facile electrochemical method involving a hydrogen coevolution cathodic electrodeposition followed by an in situ electro-oxidation process has been developed to prepare \( \varepsilon \)-MnO\(_2\) with a porous/nanoflake hierarchical architecture. Characterizations show that the cathodic-electrodeposition process produces porous spinel Mn\(_3\)O\(_4\), while the subsequent in situ electro-oxidation process rapidly and completely transforms the spinel Mn\(_3\)O\(_4\) to the \( \varepsilon \)-MnO\(_2\) in nanofoils without the destruction of the porous matrix. \( \varepsilon \)-MnO\(_2\) deposits with a porous/nanoflake hierarchical architecture have been found with a high specific capacitance of 320 F g\(^{-1}\) for the 1st cycle (0.125 F cm\(^{-2}\)) and 307 F g\(^{-1}\) for the 2000th cycle. The deposits convey an energy density of 24.4 Wh kg\(^{-1}\) at a power density of 4500 W kg\(^{-1}\). The porous manganese oxide with good and stable electrochemical performance can be the promising candidate for supercapacitors.

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consisted of a cathodic substrate centered between two parallel platinum foils (2 × 2 cm, Aldrich) as counter electrodes and an Ag/AgCl (CHI111) as the reference electrode. In the following discussions, all potentials were referred to the Ag/AgCl. The apparent area of the substrate was 1.28 cm². Particularly, a gold-disk electrode (CHI101, 2 mm diameter) was employed as the working electrode to investigate the electrochemical windows of the electrolyte. The plating solution was stirred continuously by a Teflon stirrer (Aldrich) on a hot plate during the electrochemical treatments. After deposition, the plated foils were rinsed several times in distilled water and air dried in a fume hood with reduced pressure without any further heat-treatments.

Materials characterization.— As-deposited films were characterized using X-ray diffraction (XRD, Shimadzu X-ray 6000 with Cu Kα), field-emission scanning electron microscopy (Hitachi, S-4300), transmission electron microscopy (TEM, JEOL3010) with energy dispersive X-ray spectroscopy accessory (Oxford), and X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD XPS spectrometer). Monochromated Al Kα (1486.69 eV) radiation served as the X-ray source. The pressure of the chamber was about 5 × 10⁻¹⁰ Torr during the measurement.

Electrochemical treatments and supercapacitive tests in 1.0 M sodium sulfate solution.— The as-deposited foils were then studied in a 1.0 M sodium sulfate (Aldrich) solution. Prudent observations were paid to the colors of the deposits during electrochemical treatments. The mass of the active material was obtained by weighing the dry substrate before cathodic electrodeposition and after the electrochemical measurements in the 1.0 M sodium sulfate solution at room temperature.

The supercapacitive properties of the films after electrochemical treatments were finally investigated in the same solution by cyclic voltammetry (CV), galvanostatic charge/discharge cycling, and electrochemical impedance spectroscopy (EIS) using a Solartron SI1287 electrochemical interface and a Solartron SI1260 impedance analyzer. The EIS was investigated at open-circuit potential ranging from a frequency of 10⁵ to 0.1 Hz with an ac amplitude of 5 mV.

The specific capacitance, \( C \), was calculated using the integrated area of discharge segment of the CV plot to obtain the charge, \( Q \), through the following equation

\[
C = \frac{Q}{m \Delta V} \text{F cm}^{-2} \quad C = \frac{Q}{A \Delta V} \text{F g}^{-1}
\]

where \( m \) is the mass of the active material, \( A \) is the apparent area of the substrate (1.28 cm²), and \( \Delta V \) is the potential window.

The discharge time (\( \Delta t \)) can be derived from the plot of galvanostatic charge/discharge cycling at a specific current (\( I \)). The specific capacitance was deduced from the following equation

\[
C = \frac{I \Delta t}{m \Delta V} \text{F g}^{-1}
\]

The specific power density \( (S_p) \) and specific energy density \( (S_e) \) were calculated from galvanostatic charge/discharge cycling using the following equations

\[
S_p = \frac{I \Delta V}{2m} \quad S_e = \frac{I \Delta V \Delta t}{2m}
\]

Results and Discussion

Cathodic electrodeposition.— Figure 1 shows the CV plots in 0.1 M sodium sulfate and 0.1 M sodium sulfate and 0.1 M manganese acetate aqueous solutions to verify the potential windows of the electrolytes. For both electrolytes, the dissociation of the electrolytes peaked at about −1.15 V are observed (peak a), which are associated with the evolution of \( \text{H}_2 \) gas. The shoulder peak c in Fig. 1 is attributed to the total electro-oxidation process of \( \text{Mn}^{2+} \). Finally, when the potential reaches about 1.5 V, oxygen evolution leads to the onset of peak b. The cathodic counterparts of peaks b and c result in the formation of shoulder peak d. The potential where \( \text{H}_2 \) gas forms in the present study is similar to the reported value of −1.025 V (vs Ag/AgCl). It should be mentioned that it is very difficult for the electrodeposition of Mn because of the much negative reduction potential of Mn (\( E^0 = −1.180 \) V vs normal hydrogen electrode (NHE) at 25°C) as compared with hydrogen evolution (\( E^0 = −0.828 \) V vs NHE at 25°C) based on the standard electrode potentials.

Figure 2 shows the XRD spectra of the Au-plated foil (Fig. 2a), the same foil after cathodic electrodeposition at −1.4 V for 20 min (Fig. 2b), and that after an electrochemical treatment in a 1 M sodium sulfate aqueous solution with 20 cycles of potentiodynamic potential scan between 0 and 1.0 V at 10 mV s⁻¹ (Fig. 2c). The corresponding optical photos of the foil are provided as the insets of Fig. 2. The XRD spectrum of the as-electrodeposited foil reveals the
consistent with the standard spectra of Mn$_3$O$_4$. Combining the deposits, the mean manganese oxidation state. Because a lower valence possesses separation between the two peaks 3s and 3d orbitals during the photoelectron ejection. The energy electrodeposited deposits possess a spinel Mn$_3$O$_4$ structure, which is XRD and XPS data, it can therefore be concluded that the cathodic-electrodeposited deposits. The Mn 3s XPS of the cathodic-electrodeposited deposits after cathodic electrodeposition electrochemical treatment in 1 M sodium sulfate aqueous solution is employed for cathodic-electrodeposited deposits. The Mn 3s XPS spectra for the deposits prepared after cathodic electrodeposition (−1.4 V, 20 min) and air drying and (b) after electrochemical treatment in 1 M sodium sulfate aqueous solution (20 cycles of potentiodynamic potential scan between 0 and 1.0 V at 10 mV/s).

formation of spinel Mn$_3$O$_4$ (Fig. 2b). The variation in deposition potentials and durations does not result in a significant change in the XRD patterns of the deposits. The present result is consistent with two other recent references that depicted that Mn$^{2+}$ began to precipitate to Mn(OH)$_2$ above pH 8 and the pyrochloire is very sensitive to oxygen oxidation, which leads to brown haussmanite spinel Mn$_3$O$_4$ in air drying.

XPS is employed to further specify the oxidation state of the cathodic-electrodeposited deposits. The Mn 3s XPS of the cathodic-electrodeposited deposits is shown in Fig. 3a, revealing doublet peaks due to the parallel spin coupling between the electrons in the 3s and 3d orbitals during the photoelectron ejection. The energy separation between the two peaks ($\Delta E$) is closely related to the mean manganese oxidation state. Because a lower valence possesses more electrons in the 3d orbital, more interaction can occur upon photoelectron ejection. Accordingly, $\Delta E$ would increase. From Fig. 3a, the $\Delta E$ of the Mn 3s peaks on the cathodic-electrodeposited deposits (−1.4 V, 20 min) is identified to be 5.3 eV, which is exactly consistent with the standard spectra of Mn$_3$O$_4$. Combining the XRD and XPS data, it can therefore be concluded that the cathodic-electrodeposited deposits possess a spinel Mn$_3$O$_4$ structure, which is synthesized from the oxidation of Mn(OH)$_2$ in air. The O 1s XPS spectra of the cathodic-electrodeposited deposits (not shown) showed that the deposits are hydrated.

Figure 4a-d shows the typical scanning electron microscopy (SEM) images of the porous Mn$_3$O$_4$ deposits created by cathodic electrodeposition at −1.4 V for different durations. Obviously, the pore size of the porous structure increases with the time of the deposition or the distance from the substrate. In the H$_2$ coevolution cathodic-electrodeposition process, hydrogen bubbles play a crucial role in the formation of the porous structure, which functions as a dynamic negative template, schematically illustrated in Fig. 5. The hydrogen bubbles derived from the cathodic reaction on the substrate create continuous paths from the substrate to the electrolyte–air interface during the deposition process. Hydrogen bubbles generated at different locations on the substrate result in the pores in the deposits. When electrolyzed at −1.4 V, a relatively large overpotential for hydrogen evolution, the concomitantly continuous gas evolution disrupts the diffusion of Mn$^{2+}$ from the bulk electrolyte to the ion-depleted region. As moving bubbles open up a path, the growth of deposits takes its way between gas bubbles and leave a nanowell microstructure at the top of the deposits (see Fig. 4d and e). Importantly, the pore size of the deposits increases with the distance away from the substrate due to the H$_2$ coevolution creating the structures ideally suitable for electrodes in fuel cells, batteries, sensors, and SCs. Figure 5e and corresponding TEM images in Fig. 5f and g show that the nanowalls are composed of numerous nanoparticles. The feature sizes of the nanowalls and nanoparticles are of the order of several hundreds of nanometers (in width) and 50 nm (in diameter), respectively. Figure 5g reveals the nanowell attached to nanoparticles and nanopores. The nanopores dispersed into the network of the nanoparticles are attributed to the hydrogen evolution from the freshly formed nanoparticles due to the relatively low hydrogen overpotential on the nanoparticles.

**Electrochemical treatments in 1 M sodium sulfate aqueous solution.**—The electrochemical properties of cathodic-electrodeposited Mn$_3$O$_4$ are studied through a cyclic voltammogram in a 1 M sodium sulfate aqueous solution at 10 mV/s. As shown in Fig. 6, a very broad and irreversible anodic peak instead of rectangular shapes is observed in the first CV cycle. Simultaneously, the color of the deposits becomes darker even after the first oxidative scan segment. The irreversible anodic peak disappeared after 5 cycles. Near-rectangular shapes are observed after the fifth cycle with the current increase following the increase in the cycle number. After 20 cycles, the current reaches a constant value and the color of the deposits becomes totally black (inset of Fig. 2c). This so-called “electrochemical activation process” during repeated potentiodynamic scans in the sodium sulfate aqueous solution was also reported in the CV of the Mn film and low valent manganese oxide films. According to Broughton and Brett, Mn could be electrochemically transferred to Mn$^{2+}$, Mn$_2$O$_3$, MnO$_2$, and MnO$_2$ with increasing anodic potential in the sodium sulfate aqueous solution, and the onset Mn$_2$O$_3$ exists in the potential at 0.8 V (vs Ag/AgCl) in the 1 M sodium sulfate aqueous solution. Therefore, the irreversible anodic peaks in the first 5 cycles in Fig. 5 are attributed to the electro-oxidation process from Mn$_3$O$_4$ to MnO$_2$. Because the current of the CVs becomes stable after 20 cycles, the potentiodynamic potential scan of the 20th cycle between 0 and 1.0 V at 10 mV/s in the 1 M sodium sulfate aqueous solution is employed for the electro-oxidation of the cathodic-electrodeposited Mn$_3$O$_4$ for the subsequent samples. The electro-oxidation process from cathodic-electrodeposited Mn$_3$O$_4$ to MnO$_2$ is verified by XRD (Fig. 2c) and Mn 3s XPS spectra (Fig. 3b) of the deposits after electro-oxidation. The XRD pattern in Fig. 2c shows several broad peaks with low intensity (except for the peaks attributed to the substrate), which can be assigned to e-MnO$_2$. From Fig. 3b, the $\Delta E$ of the Mn 3s peaks on the cathodic-electrodeposited deposits after electro-oxidation is 4.8 eV, which is exactly consistent with the standard spectra of MnO$_2$. The corresponding O 1s XPS spectra (not shown) indicate that the
deposits after electro-oxidation are hydrate. Based on CV, XRD, and XPS analyses, it can be concluded that the cathodic-electrodeposited hydrous spinel Mn₃O₄ is totally electro-oxidized to hydrous e-MnO₂ after 20 cycles potentiodynamic potential scans between 0 and 1.0 V at 10 mV/s in the 1 M sodium sulfate aqueous solution.

Figure 7 shows the microstructures of the electro-oxidized deposits. Comparing Fig. 7a with Fig. 4d, it is obvious that a layer of nanoflowers became dominant on the outermost surface layer of the deposits after electro-oxidation. A high magnification SEM image Fig. 7c shows that the nanoflowers are composed of many nanoflakes. Definitely, the appearance of the nanoflowers on the surface layer increases the surface area of the whole deposits. Comparing Fig. 7b with Fig. 4e, the nanoparticles on the nanowall matrices of the cathodic-electrodeposited deposits are dispelled and the petal-shaped nanoflakes are dominant without the destruction of the porous matrix after electro-oxidation. The typical TEM image Fig. 7d of the electro-oxidized deposits shows a complete disappearance of the nanoparticles with the dominance of nanoflakes. The electron diffraction pattern (inset in Fig. 7d) confirms that the deposits after electro-oxidation are e-MnO₂, which is consistent with the XRD Fig. 2c and XPS Fig. 3b measurements. The electro-oxidation process is proven to be effective to fully electro-oxidize cathodic-electrodeposited Mn₃O₄ to e-MnO₂. Importantly, the formation of a nanoflake architecture in the surface of the porous matrix without specific destruction of the porous matrix during the electro-oxidation process greatly increases the active surface area of the deposits and retains the porous matrix generated in the H₂ coevolution cathodic-electrodeposition process. It should be mentioned that the increases in both the active surface area and the Mn valence of manganese oxide deposits result in the increase in current with the increase in cycle number in Fig. 6 (electrochemical activation process) during the electro-oxidation process. Because the supercapacitive process requires the same electrolyte as the electrochemical oxidation process, the electro-oxidation can be fulfilled in situ after the capacitor is packaged. The facile in situ electro-oxidation process would greatly simplify the electrode fabrication process in the potential practical application of this method.

Supercapacitive properties measured in 1 M sodium sulfate aqueous solution.—After the in situ electro-oxidation process in a 1 M sodium sulfate aqueous solution, the supercapacitive properties of the deposits are investigated by CV. The CV plots in Fig. 8a are close to a rectangular shape and exhibit a mirror-image feature, suggesting the excellent reversibility and ideal capacitive property of the electrode. The specific capacitance values calculated from Fig. 8a.
are 320 and 307 \text{ F g}^{-1} for the 1st and 2000th cycle, respectively. The retention of 96% of its initial capacitance after 2000 cycles shows the excellent cycle capability of the deposits. The supercapacitive properties of the oxidized deposits with less mass loading are also investigated by chronopotentiometry, as shown in Fig. 9. Figure 9a shows the galvanostatic charge–discharge curves for oxidized deposits with 0.42 mg loading measured between −0.1 and 0.8 V at different current densities. The average specific capacitances calculated from Fig. 9a are found to be 348, 306, 220, and 210 \text{ F g}^{-1} for current densities of 1, 2, 5, and 10 A g\(^{-1}\), respectively. The reduction in the specific capacitance with increasing charge–discharge current density can be attributed to the low conductivity of the manganese oxide and the diffusion limitations of ions. Taking the different charge/discharge rate and electrode loading into account, the supercapacitive properties from the chronopotentiometry in Fig. 9a are consistent with those from the CVs in Fig. 8. The specific power densities and the specific energy densities can be derived from the galvanostatic charge–discharge curves in Fig. 9a. The corresponding plot of the specific power densities and the specific energy densities, which is labeled as the Ragone plot, is shown in Fig. 9b. From the Ragone plot, the oxidized deposits with a 0.42 mg loading can convey an energy density of 24.4 Wh kg\(^{-1}\) at a highest power density of 4500 W kg\(^{-1}\).

The electrochemical properties of the \(\varepsilon\)-MnO\(_2\) electrode are also studied by EIS, which is conveyed in Fig. 9c. Figure 9c shows the Nyquist plot with the semicircle over the high frequency range, followed by a straight sloped line in the low frequency region. The equivalent series resistance (ESR) of the electrode can be obtained from the \(x\) intercept of the Nyquist plot. The diameter of the semicircle corresponds to the interfacial charge-transfer resistance (\(R_{ct}\)), which is called the Faraday resistance. The ESR and \(R_{ct}\) are often the limiting factors for the power density of an SC. The EIS pattern can be fitted by an equivalent circuit,\(^{30}\) and the calculated ESR and \(R_{ct}\) of the \(\varepsilon\)-MnO\(_2\) electrode are 1.4 and 0.9 \(\Omega\). Such a low ESR and Faraday resistance could significantly facilitate the power density of the electrode. The nearly ideal straight line along the imaginary axis at the lower frequencies indicates that the electrode has a low diffusion resistance. The above EIS results confirm the excellent electrochemical capacitive properties of the prepared \(\varepsilon\)-MnO\(_2\) electrode with the porous/nanoflake hierarchical architecture.

The mass-specific capacitance (\(\text{F g}^{-1}\)) of the oxidized deposits is
fulfilled in more porous materials, a too porous architecture of an electrode is often unable to support much loading, and hence active materials tend to collapse in the electrolyte solution (poor mechanical stability), which may lead to poor area-specific capacitance and poor cycle capability. The increase in the porosity would deteriorate the conductivity of the electrode. The too porous electrode would make it difficult for the electrolyte to penetrate. The above dilemma is compromised to a great extent by our porous manganese oxides prepared via hydrogen coevolution cathodic electrodeposition incorporated with in situ electro-oxidation progress. During the cathodic-electrodeposition process, the accompanied hydrogen evolution functions as a dynamic negative template, which makes the pore size of the deposits increase with the distance away from the substrate. In the in situ electro-oxidation progress, the formation of a nanoflake architecture greatly increases the active surface area of the deposits without the destruction of the porous matrix. The final porous/nanoflake hierarchical architecture is beneficial in enhancing the supercapacitive properties of the deposits because of a number of merits and potentials. First, the relatively less porous structure existing near the substrate provides good contact between the deposits and the substrate, which decreases the ESR and increases the mechanical stability of the deposits. The relatively low ESR can enhance the supercapacitive performance in high power density. The increase in the mechanical stability provides a good cycle capability of the deposits (Fig. 8). Second, the porous/nanoflake hierarchical architecture facilitates the increase in the area-specific capacitance of the electrode without specific compromising of the mass-specific capacitance. This character is provided in Fig. 8, which shows that the deposits can convey a relatively high area-specific capacitance of 0.125 F cm⁻² and can keep a relatively high mass-specific capacitance of 320 F g⁻¹. Lastly, the open-porous architecture generated from the cathodic electrodeposition is propitious to the rapid and complete electro-oxidation of the deposits, which definitely simplifies the electro-oxidation process.

Conclusions

A e-MnO₂ with a porous/nanoflake hierarchical architecture has been synthesized by hydrogen coevolution cathodic electrodeposition incorporated with an in situ electro-oxidation progress. The product synthesized by a cathodic-electrodeposition process is porous spinel Mn₃O₄. During the cathodic-electrodeposition process, the accompanied hydrogen evolution functions as a dynamic negative template, which makes the pore size of the deposits increase with the distance away from the substrate. In the in situ electro-oxidation progress rapidly and completely enables the transformation of the haussmanite spinel Mn₃O₄ into the e-MnO₂ in nanoflakes without the destruction of the porous matrix. Such e-MnO₂ deposits with a porous/nanoflake hierarchical architecture possess a high specific capacitance of 320 F g⁻¹ for the 1st cycle (0.125 F cm⁻²) and 307 F g⁻¹ for the 2000th cycle. The deposited MnO₂ possesses an energy density of 24.4 Wh kg⁻¹ at a power density of 4500 W kg⁻¹. The porous manganese oxides with good and stable electrochemical performances can be the promising candidates for SCs.

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