Electronic supplementary information (ESI†) for

Designing Thermal and Electrochemical Oxidation Processes for δ-MnO₂ Nanofibers for High-performance Electrochemical Capacitors

Ji-Hoon Lee,¹ Tae-Youl Yang,¹ Ho-Young Kang,¹ Dae-Hyun Nam,¹ Na-Rae Kim,¹
Yoo-Yong Lee,¹ Se-Hee Lee,² and Young-Chang Joo*¹

¹Department of Materials Science & Engineering, Seoul National University, Seoul 1151-744, Korea

²Department of Mechanical Engineering, University of Colorado at Boulder, Boulder, CO 80300-0427, USA

AUTHOR INFORMATION

Corresponding Author

Young-Chang Joo (ycjoo@snu.ac.kr, Tel.: +82-2-880-8986, Fax.: +82-2-883-8197)
1. Effect of the manganese precursor and organic matrix on the morphology of the NFs

![Fig. S1](image)

<table>
<thead>
<tr>
<th>Manganese precursors</th>
<th>As-spun NFs</th>
<th>Thermally calcined NFs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn acetylacetonate (10 wt.%) + PVAc (15 wt.%)</td>
<td>![Image A]</td>
<td>![Image B]</td>
</tr>
<tr>
<td>Mn acetylacetonate (10 wt.%) + PVP (15 wt.%)</td>
<td>![Image C]</td>
<td>![Image D]</td>
</tr>
<tr>
<td>Mn nitrate (10 wt.%) + PVP (15 wt.%)</td>
<td>![Image F]</td>
<td>![Image G]</td>
</tr>
</tbody>
</table>

Fig. S1 FE-SEM and TEM images of the as-spun and thermally calcined MnO₅ NFs fabricated with various Mn-precursor species and organic matrix materials (the solution compositions are listed on the left side, and all the NFs were spun with 10 g of DMF and 0.8 ml of acetic acid). The thermal calcination conditions were the same for all the samples (300 °C for 3 h in air with a ramping rate of 3 °C/min).

<table>
<thead>
<tr>
<th>Manganese precursors</th>
<th>Manganese (III) acetylacetonate</th>
<th>Manganese (II) nitrate tetrahydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
<td>Mn(C₅H₇O₂)₃</td>
<td>Mn(NO₃)₂·4H₂O</td>
</tr>
<tr>
<td>Linear formula</td>
<td>Mn(C₅H₇O₂)₃</td>
<td>Mn(NO₃)₂·4H₂O</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>352.26 g/mol</td>
<td>251.01 g/mol</td>
</tr>
<tr>
<td>Melting point</td>
<td>159 ~ 161 °C</td>
<td>37 °C</td>
</tr>
</tbody>
</table>

Table S1 Material properties of the manganese precursors used in this study.
Organic matrices

<table>
<thead>
<tr>
<th>Materials</th>
<th>Polyvinylpyrrolidone (PVP)</th>
<th>Poly(vinyl acetate) (PVAc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear formula</td>
<td>((C_6H_9NO)_n)</td>
<td>([CH_2CH(O_2CCH_3)]_n)</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>(~1,300,000)</td>
<td>(~500,000)</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>(~175 , ^\circ C) (^2)</td>
<td>(30 , ^\circ C) (^3)</td>
</tr>
</tbody>
</table>

Table S2 Material properties of the organic matrices used in this study.

Fig. S1 shows the effect of the Mn-precursor species and organic matrix materials on the morphology of the Mn oxide NFs after thermal calcination. The weight fractions in the electrospinning solution and thermal calcination conditions are described in Fig. S1. The morphologies of the as-spun NFs (Figs. S1A, C, and F) are similar, i.e., they have the same average widths and areal densities. Spreading, collapse, and an increase in the NF width were observed when polyvinyl acetate (PVAc) was used as the organic matrix material (Fig. S1B). The low glass transition temperature of the organic matrix was responsible for the morphological changes (Table S1). During thermal calcination, especially when the temperature was above \(~30 \, ^\circ C\), PVAc transformed into a glassy state that exhibited significant viscous flow. A comparison of Figs. S1D and G reveals that the Mn-nitrate-based NFs exhibited leaf-like surface morphologies with a high degree of roughness after thermal calcination, while the Mn-acetylacetonate-based NFs exhibited a smooth, straight 1-D structure. In addition, as observed in Figs. S1E and H, the Mn-nitrate-based NFs contained spindle-shaped grains that were larger than those of the Mn-acetylacetonate-based NFs. Because the melting point of Mn nitrate is much lower than that of Mn acetylacetonate, the grains agglomerated easily and developed rough surfaces. Therefore, the Mn acetylacetonate + PVP-based MnO\(_x\) NFs were used for further investigation because of their smaller grain size, which resulted in a high surface area and was beneficial for high structural integrity.
3. Effect of the solution composition, $P_{O_2}$, and calcination temperature

Fig. S2 (A) Phase map for the thermally calcined MnO$_x$ NFs as a function of the mass ratio (mass of oxygen ($m_0$)/mass of manganese ($m_{Mn}$) loaded in the as-spun NFs) and $P_{O_2}$ used during the calcination process. The composition of the top line (1 and 2): Mn acetylacetonate (10 wt. %) + PVP (16 wt. %), middle line (3 ~ 7): Mn acetylacetonate (10 wt. %) + PVP (15 wt. %), and bottom line (8 and 9): Mn nitrate tetrahydrate (10 wt. %) + PVP (15 wt. %). (B) Corresponding XRD patterns. All the NFs were thermally calcined at 300 °C for 3 h with a ramping rate of 3 °C/min.
Fig. S3 FE-SEM (A) and TEM (B) images and XRD pattern (C) of MnOₓ NFs thermally calcined at 500 °C for 3 h in ambient air. The electrospinning solution composition was Mn acetylacetonate (10 wt. %) + PVP (15 wt.%).

Fig. S2A shows the crystallographic phases of various manganese oxide NFs fabricated from solutions with various material species, compositions, and Pₒ₂ levels for thermal calcination. The m₀/mₘn ratio was calculated based on the following assumption: DMF, acetic acid, and the hydrous component of the manganese precursor were completely evaporated during electrospinning. The phase of thermally calcined manganese oxide NF transformed from Mn₃O₄ to Mn₂O₃ as the m₀/mₘn ratio and Pₒ₂ level increased. However, the phases were limited to a single phase or mixture of low-valence MnOₓ (x < 2). Fig. S2B presents the corresponding XRD patterns.

The starting phase of the MnOₓ NFs was also dependent on the calcination temperature, as observed in Fig. S3. When the composition of the electrospinning solution was Mn acetylacetonate (10 wt. %) + PVP (15 wt.%), the crystallographic phase of the MnOₓ NFs after calcination at 300 and 500 °C in air were Mn₃O₄ and Mn₂O₃, respectively. According to phase transformation studies on MnO₂ powders, with increasing temperature, ⁴,⁵ the MnO₂ phase was transformed into Mn₂O₃ (above ~ 470 °C) ⁴, and the Mn₃O₄ phase was finally obtained at 1000 °C ⁵ due to the release of oxygen from the manganese dioxide lattice. Due to the existence of many of the organic materials in the as-spun NFs, the transformation procedure and stable phase at certain conditions (temperature and Pₒ₂) was significantly different from the known world of metallurgy. Based on the above experimental result, it was confirmed that manganese
oxide NFs with the MnO$_2$ phase are difficult to produce using the thermal calcination process even when the composition of the electrospinning solution is changed.
3. Decomposition behavior of organic contents in as-spun NFs

Fig. S4 Thermogravimetric analysis (TGA) curves for as-spun MnO$_x$ NFs (Mn-acetylacetonate + PVP) conducted with a heating rate of 10 °C/min under ambient air (temperature range: 35 to 700 °C).
4. Oxidation behavior of MnOₓ NFs under CV

**Fig. S5** Cyclic voltammogram of the first 2 cycles of the thermally calcined MnₓO₄ (A) and MnₓO₃ (B) NFs. pₓ₁, pₓ₂, and pₓ₁ indicate the 1st anodic, 2nd anodic and 1st cathodic current peaks, respectively.

**Fig. S6** Cyclic voltammogram of the first 2 cycles for carbon fiber paper (CFP).

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Anodic peak potential</th>
<th>Cathodic peak potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermally calcined Mn₃O₄</td>
<td>0.73</td>
<td>0.95</td>
</tr>
<tr>
<td>Thermally calcined Mn₂O₃</td>
<td>0.74</td>
<td>0.96</td>
</tr>
</tbody>
</table>

**Table S3** Peak potentials measured from the 1st CV of the thermally calcined Mn₃O₄ and Mn₂O₃.
Cyclic voltammetry measurements of MnOx NFs were conducted in the potential range of 0 ~ 1.1 V with a scan rate of 2 mV/s. The first 2 cycles are depicted in Figs. S5A and B. Both CVs of the MnOx NFs revealed 2 anodic peaks and 1 cathodic peak at nearly the same potential (Table S3); however, the NFs had different peak current densities. By investigating the CV of CFP as a current collector (Fig. S6), it is confirmed that the current peaks observed in the CVs in Figs. S5A and B were solely related to the electrochemical oxidation of the MnOx NFs. Furthermore, the potential peaks are consistent with the plateau potentials in Fig. 2A. The electrochemical reaction (1), which is related to $p_{a1}$ and $p_{a1}'$, was kinetically fast and spontaneous because it was terminated after only 1 cycle, as demonstrated by the disappearance of the 1st anodic peak in the 2nd CV (Fig. S5). The current density of the 2nd anodic peak of the 1st cycle was slightly reduced compared with that of the 2nd cycle for both of the thermally calcined NFs. This result indicates that the amount of Mn$^{3+}$ transformed into Mn$^{4+}$ gradually decreased with increasing cycle number. Several causes for the decrease in the peak current density with cycling are possible. First, some of the reduced, soluble low-valence Mn ions formed during the successive cathodic potential scan were dissolved from the electrode, preventing their involvement in the 2nd oxidation process of the next cycle. Second, the Mn$^{4+}$ ions generated during a given cycle did not contribute to the 2nd anodic peak of the next cycle. It is indirectly indicated that CV oxidation could not complete the MnO$_x$ phase transformation.
5. Comparison of the amount of dissolved Mn ions during galvanostatic oxidation and CV oxidation

![Fig. S7](image)

Fig. S7 Photographs of thermally calcined Mn$_3$O$_4$ after 1000 CV cycles (A) and G-oxidized Mn$_3$O$_4$ after galvanostatic oxidation (B) and 1000 CV cycles (C).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Na (mg/L)</th>
<th>Mn (mg/L)</th>
<th>Mn/Na (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>40576</td>
<td>8.750</td>
<td>0.0216</td>
</tr>
<tr>
<td>B</td>
<td>41386</td>
<td>0.472</td>
<td>0.0011</td>
</tr>
<tr>
<td>C</td>
<td>41401</td>
<td>2.420</td>
<td>0.0058</td>
</tr>
</tbody>
</table>

Table S4 The Mn/Na ratio in the electrolyte of the thermally calcined Mn$_3$O$_4$ after 1000 CV cycles and the G-oxidized Mn$_3$O$_4$ after galvanostatic oxidation and 1000 CV cycles measured by ICP-OES. (A)-(C) correspond to the samples depicted in Fig. S7.
6. XPS Mn 3s core level survey spectra of thermally calcined and G-oxidized MnOₓ NFs

![Image of XPS spectra]

**Fig. S8** The detected XPS Mn 3s core level survey spectra (black line) and deconvoluted spectra for the upper (blue dashed line) and lower binding energy peak (red dashed line) of the thermally calcined Mn₃O₄ (A) and Mn₂O₃ (B) NFs and the G-oxidized Mn₃O₄ (C) and Mn₂O₃ (D) NFs. Deconvolution was performed using the Gaussian distribution fitting.
7. Calculation of the oxidation, capacitive, and oxygen evolution reaction (OER) charge fractions

**Fig. S9** Linear sweep voltammograms of the thermally calcined Mn$_3$O$_4$ (A) and Mn$_2$O$_3$ (B) NFs positively scanned from their open circuit potential (OCP) to 1.3 V vs. SCE. Cyclic voltammograms of the thermally calcined Mn$_3$O$_4$ (C) and Mn$_2$O$_3$ (D) NFs with a potential range between 0.2 and 0.5 V vs. SCE, revealing no faradaic electrochemical reactions.
**Separation of the OER charge**

The standard electrode potential of OER for this system was 0.62 V vs. SCE when the pH of the 1 M Na$_2$SO$_4$ (aq) solution used in this study was 6.2. Therefore, the oxidation potentials of the low-valence MnO$_x$ NFs overlapped with that of the OER process. According to the Tafel equation, the log of the response current has a linear dependence on the overpotential at high overpotentials. Therefore, the factors related to the OER process was evaluated using the Tafel plot. The Tafel equation for the OER process and corresponding electrochemical reaction are given below.

\[
\ln(i_{\text{net}}) = \ln(i_{\text{OER}}) = \ln(i_0) + \frac{(1 - \alpha)nF}{2.3RT} \eta_{\text{OER}} \quad (\text{for } \eta_{\text{OER}} \gg 0)
\]

\[
H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-
\]

where, $i_{\text{net}}$ is the difference between the anodic and cathodic currents and $i_0$ is the exchange current. $\alpha$, $n$, and $\eta_{\text{OER}}$ are the symmetric factor, number of electron moles used in OER, and OER overpotential, respectively. $F$, $R$, and $T$ have their common meanings. Fig. S9A and B show the total current density and corresponding OER current density for thermally calcined Mn$_3$O$_4$ and Mn$_2$O$_3$, respectively.

**Separation of the capacitive charge**

To calculate the capacitive portion during the oxidation process, the MnO$_x$ NFs were cycled within a potential range of 0.2 ~ 0.5 V (Fig. S9C and D), where no signals related to faradaic electrochemical reactions were observed in the linear sweep voltammetry curve (Fig. S9A and B). It is assumed that the capacitance evaluated in the potential region of 0.2 - 0.5 V exhibited pure capacitive behavior and was independent of the electrode potential according to its original definition.

**Calculation of each charge fraction**
The definitions of each charge component involved in the galvanostatic oxidation of the low-valence MnOₓ NFs from their open circuit potential (OCP) to a given electrode potential are presented below.

\[ f_{\text{capacitive}} = \frac{Q_{\text{capacitive}}}{Q_{\text{total}}} \quad f_{\text{OER}} = \frac{Q_{\text{OER}}}{Q_{\text{total}}} \quad f_{\text{oxidation}} = \frac{Q_{\text{oxidation}}}{Q_{\text{total}}} \]  

(3)

\[ f_{\text{capacitive}} + f_{\text{OER}} + f_{\text{oxidation}} = 1 \]  

(4)

\[ f_{\text{capacitive}} = \frac{F_{\text{capacitive}} \times (V - \text{OCP})}{\int_{\text{OCP}}^{V} t_{\text{total}}/g \ dV}, \quad (\text{where, } F_{\text{capacitive}} = \frac{\int i_{\text{capacitive}}/g \ dV}{2 \times \Delta V \times v}) \]  

(5)

\[ f_{\text{OER}} = \frac{\int_{\text{OCP}}^{V} i_{\text{OER}}/g \ dV}{\int_{\text{OCP}}^{V} t_{\text{total}}/g \ dV} \]  

(6)

where \( Q_{\text{capacitive}} \), \( Q_{\text{OER}} \), and \( Q_{\text{oxidation}} \) are the capacitive, OER, and oxidation charges, respectively. OCP, \( v \), and \( g \) are the open circuit potential, scan rate, and mass of the total electrode, respectively.
8. Notes and References


