Facile Synthesis of Co$_3$O$_4$/CoF$_2$·4H$_2$O/graphene Composites for Supercapacitor Electrodes

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Received: 10 July 2018 / Accepted: 11 September 2018 / Published: 1 October 2018

Co$_3$O$_4$/CoF$_2$·4H$_2$O/graphene composites and Co$_3$O$_4$/graphene composites are synthesized by a facile microwave-assisted hydrothermal synthesis, followed by calcining at 350 °C. The synthesized composites are characterized by X-ray diffraction, and scanning electron microscopy. Electrochemical property of the prepared composites is measured by cyclic voltammetry and galvanostatic charge-discharge. Results show that Co$_3$O$_4$/CoF$_2$·4H$_2$O/graphene composites exhibit better specific capacitance and retention ratio of initial specific capacitance when compared with Co$_3$O$_4$/graphene composites. Particularly, Co$_3$O$_4$/CoF$_2$·4H$_2$O/graphene composites prepared using CoSO$_4$·7H$_2$O as material exhibit the highest specific capacitance at various current densities, retention ratio of the specific capacitance at the current density ranging from 1 to 4 A g$^{-1}$ and retention ratio of initial specific capacitance after 1000 cycles, indicating excellent rate capability and cycling stability. These characteristics demonstrate that Co$_3$O$_4$/CoF$_2$·4H$_2$O/graphene composites prepared using CoSO$_4$·7H$_2$O as material possess a great potential application in supercapacitors.

Keywords: Supercapacitors, Co$_3$O$_4$, CoF$_2$·4H$_2$O, graphene

1. INTRODUCTION

Recently, supercapacitors in virtue of high power density, rapid charge-discharge capability, and excellent long cycle performance, have been receiving more and more attention. The properties of supercapacitors are mostly decided by the characteristics of electrode materials. Therefore, there are increasing literatures about electrode materials applied as supercapacitors. Electrode materials including but not limited to carbon materials [1-3], transition metal oxides [4-9], transition metal sulfides [10, 11], conducting polymers [12, 13] and their composites [14-16] have been used in supercapacitors. Co$_3$O$_4$ as transition metal oxides, due to its high redox activity, low cost, environmental safety and ultrahigh theoretical specific capacitance (3560 F g$^{-1}$), is a promising
electrode material as supercapacitors. Xiao et al. synthesized 3D hierarchical Co$_3$O$_4$ twin-spheres, which exhibits a specific capacitance of 781 F g$^{-1}$ at 0.5 A g$^{-1}$ [17]. Co$_3$O$_4$ thin film prepared by a chemical bath deposition method delivers a high specific capacitance of 227 F g$^{-1}$ at 0.2 A g$^{-1}$ [4]. However, Co$_3$O$_4$ investigated above possesses the limited capacitance, which is much less than its theoretical specific capacitance. This is because of its low electron conductivity and poor durability in the charge-discharge processes. To overcome these problems, an efficient strategy is introduce carbon materials in Co$_3$O$_4$. Graphene, as carbon materials, has been widely used in supercapacitors due to its excellent electronic conductivity, outstanding mechanical flexibility and large surface area [18, 19].

Many approaches are available for synthesizing Co$_3$O$_4$/graphene composites for supercapacitors. Park et al. reported that Co$_3$O$_4$/graphene composites with carbon blacks filler addition (15 wt.%) delivered a specific capacitance of 341 F g$^{-1}$ at 10 mV s$^{-1}$ [20]. Guan et al. synthesized needle-like Co$_3$O$_4$/graphene composites, which showed a specific capacitance of 157.7 F g$^{-1}$ at 0.1 A g$^{-1}$ [19]. We utilized a hydrothermal method to synthesize Co$_3$O$_4$/graphene composites, which showed a specific capacitance of 1033.4 F g$^{-1}$ at 0.2 A g$^{-1}$ [21]. Yang et al. synthesized oxygen-vacancy Co$_3$O$_4$/graphene composites, which showed remarkable rate capability and long-term cycle stability [14]. However, there are only few reports on the preparation of Co$_3$O$_4$/graphene composites by addition of CoF$_2$·4H$_2$O to increase their performance of supercapacitors.

Herein, we proposed a facile microwave-assisted hydrothermal synthesis to prepare Co$_3$O$_4$/CoF$_2$·4H$_2$O/graphene composites for the first time. For comparison, Co$_3$O$_4$/graphene composites were synthesized by the same method. More significantly, Co$_3$O$_4$/graphene composites were synthesized using Co(CH$_3$COO)$_2$·4H$_2$O and graphite oxide as material. However, Co$_3$O$_4$/CoF$_2$·4H$_2$O/graphene composites were obtained only using Co(NO$_3$)$_2$·6H$_2$O or CoSO$_4$·7H$_2$O instead of Co(CH$_3$COO)$_2$·4H$_2$O under the same condition. Furthermore, complex synthetic routes, which were costly and time consuming, were not involved in the synthesis of Co$_3$O$_4$/CoF$_2$·4H$_2$O/graphene composites. Electrochemical studies demonstrated effects of CoF$_2$·4H$_2$O on capacitive performances of the composites. Results showed that Co$_3$O$_4$/CoF$_2$·4H$_2$O/graphene composites exhibited larger specific capacitance than those of Co$_3$O$_4$/graphene composites at various current densities. It implied that introducing CoF$_2$·4H$_2$O in Co$_3$O$_4$/graphene composites to obtain Co$_3$O$_4$/CoF$_2$·4H$_2$O/graphene composites was an efficient strategy to improve their capacitive performance.

2. EXPERIMENTAL

2.1. Materials Synthesis

Co$_3$O$_4$/CoF$_2$·4H$_2$O/graphene composites were prepared by a facile microwave-assisted hydrothermal synthesis. The synthesis process is as follows. 80 mg of graphite oxide was added in 70 mL of deionized water with sonication. Then, 4 mmol of Co(NO$_3$)$_2$·6H$_2$O or CoSO$_4$·7H$_2$O, 30 mmol of CO(NH$_2$)$_2$, and 12 mmol of NH$_4$F were dissolved into above solution under constant magnetic stirring. Afterwards, the obtained solution was transferred to a double-walled digestion vessel, sealed
and thermally treated at 150 °C for 15 min using a microwave digestion system (MDS-6G, SINEO). After naturally cooling down to room temperature, the obtained precipitates were collected, washed 3 times with deionized water and absolute ethanol, and then dried at 60 °C for 12 h. Finally, the as-prepared powder was calcinated at 350 °C for 3 h to obtain Co₃O₄/CoF₂·4H₂O/graphene composites. Co₃O₄/CoF₂·4H₂O/graphene composites synthesized with Co(NO₃)₂·6H₂O as material were denoted as Co₃O₄/CoF₂·4H₂O/G-1. Co₃O₄/CoF₂·4H₂O/graphene composites prepared with CoSO₄·7H₂O as material were referred to as Co₃O₄/CoF₂·4H₂O/G-2. Co₃O₄/graphene composites, designated as Co₃O₄/G, were synthesized by a microwave-assisted hydrothermal synthesis with 4 mmol of Co(CH₃COO)₂·4H₂O instead of 4 mmol of Co(NO₃)₂·6H₂O or CoSO₄·7H₂O under the same condition.

2.2. Materials Characterization

The structure of as-obtained products was investigated by X-ray diffraction (XRD, Bruker, D8-Advance). The morphology of as-obtained products was observed by scanning electron microscopy (Hitachi SU8000).

2.3. Electrochemical measurements

Electrochemical studies of the as-prepared electrodes were evaluated by cyclic voltammetry (CV), and galvanostatic charge–discharge. All electrochemical measurements were performed on a CHI 660D electrochemical workstation with a three-electrode cell at room temperature. 2 M KOH solution was used as the electrolyte. The working electrode was fabricated as follows. 80 wt % of the as-prepared composites as active material, 15 wt % of acetylene black as conductive agent, and 5 wt % poly(tetrafluoroethylene) as binder were first mixed to form a slurry. Then, the slurry was pasted on a nickel foam substrate (1 cm × 1 cm) with a spatula and dried naturally. Finally, the electrode was pressed at 10 Mpa and dried at 110 °C for 12 h under vacuum. A Pt plate and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

3. RESULTS AND DISCUSSION

3.1. XRD analyses

Fig. 1 shows XRD patterns of Co₃O₄/G, Co₃O₄/CoF₂·4H₂O/G-1 and Co₃O₄/CoF₂·4H₂O/G-2. All the peaks in curve 1a can be indexed to Co₃O₄ (JCPDS No. 42-1467) and graphene [21-23]. The characteristic peaks of Co₃O₄ (JCPDS No. 42-1476), CoF₂·4H₂O (JCPDS No. 40-0627) and graphene are detected in in curves 1b and 1c. The positions of the XRD peaks in curves 1b and 1c are consistent. However, the peak width at half maxima intensity in curves 1b is larger than that in curves 1c, except for characteristic peak of graphene. According to Scherrer formula [24], the crystallite sizes of Co₃O₄ and CoF₂·4H₂O can be estimated. Therefore, the crystallite sizes of Co₃O₄ and CoF₂·4H₂O in Co₃O₄/CoF₂·4H₂O/G-1 synthesized with Co(NO₃)₂·6H₂O as material are larger than that of
Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 prepared with CoSO$_4$·7H$_2$O as material. These results indicate distinct impact of cobalt salt type on the phase composition and the crystallite sizes of as-synthesized products.

**Figure 1.** XRD patterns of Co$_3$O$_4$/G (a), Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 (b) and Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 (c).

### 3.2. Morphology

**Figure 2.** SEM images of Co$_3$O$_4$/G (a, b), Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 (c, d) and Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 (e, f).
SEM images of Co$_3$O$_4$/G, Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 and Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 are displayed in Fig. 2. For Co$_3$O$_4$/G (Fig. 2a and 2b), nanoplates together with some irregular agglomerates composed of a great of nanoparticles is Co$_3$O$_4$ and crumpled structure is graphene. For Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 (Fig. 2c-d) and Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 (Fig. 2e-f), Co$_3$O$_4$ and CoF$_2$·4H$_2$O with structure of nanoplates and some irregular agglomerates are observed. Graphene with crumpled structure is also found. However, there are some different morphologies in Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 and Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2. A major difference is that thinner nanoplates exist in Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2. Thinner nanoplates can be in favour of the penetration of the electrolyte, leading to improve capacitive properties of material.

3.3. Electrochemical capacitor property

Fig. 3 displays cyclic voltammograms of Co$_3$O$_4$/G electrode, Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 electrode and Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 electrode at a scan rate of 5 mV s$^{-1}$. The shape of the CV curves exhibits pseudocapacitive behaviour, which originates from Faradaic reactions. Within the potential scanning range, two redox peaks are observed. In Co$_3$O$_4$/G electrode, the redox peaks correspond to Faradaic redox reactions as follows [14, 25].

$$\text{CoOOH} + \text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^- \quad (1)$$
$$\text{Co}_3\text{O}_4 + \text{H}_2\text{O} + \text{OH}^- \leftrightarrow 3\text{CoOOH} + e^- \quad (2)$$

However, except for above Faradaic redox reactions, the following reaction exists in Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 electrode and Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 electrode [26].

$$\text{CoF}_2 + 3\text{OH}^- \leftrightarrow \text{CoOOH} + \text{H}_2\text{O} + 2\text{F}^- + e^- \quad (3)$$

In Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 electrode and Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 electrode, only two redox peaks rather than three redox peaks are observed. This is because redox reaction (2) and redox reaction (3) are ascribable to Faradaic redox reaction of Co$^{3+}$/Co$^{2+}$.

![Figure 3. Cyclic voltammograms of Co$_3$O$_4$/G electrode (a), Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 electrode (b) and Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 electrode (c) at a scan rate of 5 mV s$^{-1}$.](image)

Among three electrodes, the order of the enclosed area of the CV curves ranks from low to high: Co$_3$O$_4$/G electrode, Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 electrode, Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 electrode. As we all know, the specific capacitance is proportional to the enclosed area of the CV curve [24, 27, 28].
Therefore, the specific capacitance of Co$_3$O$_4$/CoF$_2$-4H$_2$O/G-2 electrode is the highest, the second is Co$_3$O$_4$/CoF$_2$-4H$_2$O/G-1 electrode, and the specific capacitance of Co$_3$O$_4$/G electrode is much lower than those of the other two electrodes. This is in agreement with the result of the following charge-discharge measurements. It can be explained as follows. Synergistic effect of Co$_3$O$_4$, CoF$_2$-4H$_2$O and graphene exists in Co$_3$O$_4$/CoF$_2$-4H$_2$O/G-1 or Co$_3$O$_4$/CoF$_2$-4H$_2$O/G-2 when compared with Co$_3$O$_4$/G. Besides, the favorable structure and morphology of Co$_3$O$_4$/CoF$_2$-4H$_2$O/G-2 provides better ion accessibility when compared with Co$_3$O$_4$/CoF$_2$-4H$_2$O/G-1 and Co$_3$O$_4$/G.

![Cyclic voltammograms](image)

**Figure 4.** Cyclic voltammograms of Co$_3$O$_4$/G electrode (a), Co$_3$O$_4$/CoF$_2$-4H$_2$O/G-1 electrode (b) and Co$_3$O$_4$/CoF$_2$-4H$_2$O/G-2 electrode (c) in a potential range from -0 to 0.5 V at different scan rates.

Fig. 4 shows cyclic voltammograms Co$_3$O$_4$/G electrode, Co$_3$O$_4$/CoF$_2$-4H$_2$O/G-1 electrode and Co$_3$O$_4$/CoF$_2$-4H$_2$O/G-2 electrode in a potential range from -0 to 0.5 V at scan rates from 5 to 50 mV s$^{-1}$. The shape of all the curves further signifies the pseudocapacitive behaviour, which corresponds to Faradaic redox reactions of Co$^{3+}$/Co$^{4+}$ and Co$^{3+}$/Co$^{4+}$ [29]. Among three electrodes, the peak current density and enclosed area of the CV curves gradually increase with increasing scan rate. Moreover, the anodic peak potential shifts to higher value and the cathodic peak potential shifts to lower value when increasing scan rate, respectively. This can be due to the polarization effect of the electrode.
Figure 5. Galvanostatic charge-discharge curves of Co$_3$O$_4$/G electrode (a), Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 electrode (b) and Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 electrode (c) at different densities.

Figure 6. Relationship between the specific capacitance and the current density of Co$_3$O$_4$/G electrode, Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 electrode and Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 electrode.

Fig. 5 depicts galvanostatic charge–discharge curves of Co$_3$O$_4$/G electrode, Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-1 electrode and Co$_3$O$_4$/CoF$_2$·4H$_2$O/G-2 electrode at the current densities of 1, 2, 3 and 4 A g$^{-1}$. The shape of the charge-discharge curves shows the characteristics of pseudocapacitance
caused by Faradaic reactions, which substantiates the results of the CV curves. The specific capacitance of the electrode can be calculated from the discharge curves according to the following equation [28, 30-33].

\[ C_{sp} = \frac{I}{V_m t} \]  

(4)

where \( C_{sp} \) is the specific capacitance (F g\(^{-1}\)), \( I \) indicates the discharge current (A), \( t \) represents the discharge time (s), \( V \) stands for the potential change during discharge, \( m \) is the mass of active material, respectively.

**Table 1.** Comparison of similar electrode materials in literatures with this study.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Electrolyte</th>
<th>Current density or scan rate</th>
<th>Specific capacitance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Co}_3\text{O}_4/\text{graphene} )</td>
<td>2M KOH</td>
<td>0.1 A g(^{-1})</td>
<td>157.7 F g(^{-1})</td>
<td>[19]</td>
</tr>
<tr>
<td>( \text{Co}_3\text{O}_4/\text{graphene} )</td>
<td>6M KOH</td>
<td>10 mV s(^{-1})</td>
<td>341 F g(^{-1})</td>
<td>[20]</td>
</tr>
<tr>
<td>( \text{Co}_3\text{O}_4/\text{graphene} )</td>
<td>2M KOH</td>
<td>0.2 A g(^{-1})</td>
<td>1033.4 F g(^{-1})</td>
<td>[21]</td>
</tr>
<tr>
<td>( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{graphene} )</td>
<td>2 M KOH</td>
<td>1 A g(^{-1})</td>
<td>237.7 F g(^{-1})</td>
<td>This work</td>
</tr>
<tr>
<td>( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{graphene} ) (Co(NO(_3))(_2)-6H(_2)O as material)</td>
<td>2 M KOH</td>
<td>1 A g(^{-1})</td>
<td>241.8 F g(^{-1})</td>
<td>This work</td>
</tr>
</tbody>
</table>

Based on the equation (4), the specific capacitance of \( \text{Co}_3\text{O}_4/\text{G} \) electrode, \( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{G}-1 \) electrode and \( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{G}-2 \) electrode at different current densities is shown in Fig. 6. The specific capacitance of three electrodes follows the following descending order: \( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{G}-2 \) electrode, \( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{G}-1 \) electrode, \( \text{Co}_3\text{O}_4/\text{G} \) electrode. This is in accordance with the CV results. The specific capacitance of \( \text{Co}_3\text{O}_4/\text{G} \) electrode, \( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{G}-1 \) electrode and \( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{G}-2 \) electrode at 1 A g\(^{-1}\) are 77.5, 237.7 and 241.8 F g\(^{-1}\), respectively. Compared with \( \text{Co}_3\text{O}_4/\text{G} \) electrode, the specific capacitance of \( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{G}-1 \) electrode and \( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{G}-2 \) electrode at 1 A g\(^{-1}\) is 3.07 times and 3.12 times, respectively. This manifests that \( \text{Co}_3\text{O}_4/\text{graphene} \) composites by addition of \( \text{CoF}_2\cdot\text{4H}_2\text{O} \) can greatly enhance their performance of supercapacitors. The reason for this has been explained in analyzing the specific capacitance according to the CV curves. A comparison of similar electrode materials in literatures with this study was shown in Table 1. The specific capacitance values of \( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{G}-1 \) electrode (237.7 F g\(^{-1}\) at 1 A g\(^{-1}\)) and \( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{G}-2 \) electrode (241.8 F g\(^{-1}\) at 1 A g\(^{-1}\)) are much higher than that of reported \( \text{Co}_3\text{O}_4/\text{graphene} \) composite electrode (157.7 F g\(^{-1}\) at 0.1 A g\(^{-1}\)) [19]. They are not as high as those of \( \text{Co}_3\text{O}_4/\text{graphene} \) composite electrode [20, 21]. However, in this work, \( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{G}-1 \) and \( \text{Co}_3\text{O}_4/\text{CoF}_2\cdot\text{4H}_2\text{O}/\text{G}-2 \) are synthesized with microwave-assisted hydrothermal synthesis, which were a short consuming-time (15 min). Besides, this work provides a method to enhance the specific capacitance of transition metal oxides/graphene composite. When the
current density increases to 4 A g\(^{-1}\), Co\(_3\)O\(_4\)/G electrode, Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-1 electrode and Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-2 electrode show a specific capacitance retention of 95.0%, 80.2% and 97.1%, respectively. It implies that Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/graphene composites prepared with CoSO\(_4\)-7H\(_2\)O as material exhibits excellent rate capability. Although the retention ratios of the specific capacitance for Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-1 electrode is the lowest, the specific capacitance of Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-1 electrode at 4 A g\(^{-1}\) is 2.59 times higher than that of Co\(_3\)O\(_4\)/G electrode.

The cycling stability of Co\(_3\)O\(_4\)/G electrode, Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-1 electrode and Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-2 electrode is evaluated by galvanostatic charge–discharge tests at the current density of 1 A g\(^{-1}\) and the results are shown in Figure 7. After 1000 cycles, the specific capacitance retention of Co\(_3\)O\(_4\)/G electrode, Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-1 electrode and Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-2 electrode is 91.5%, 94.6% and 95.2%, respectively. It indicates that Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-1 electrode and Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-2 electrode show better cycling stability than Co\(_3\)O\(_4\)/G electrode. The specific capacitance retention of Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-1 electrode and Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-2 electrode higher than that of previously reported Co\(_3\)O\(_4\)/graphene electrode [19-21].

![Figure 7. Cycling performance of Co\(_3\)O\(_4\)/G electrode, Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-1 electrode and Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/G-2 electrode at the current density of 1 A g\(^{-1}\).](image)

4. CONCLUSIONS

A microwave-assisted hydrothermal has been successfully developed for the synthesis of Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/graphene composites and Co\(_3\)O\(_4\)/graphene composites. The specific capacitance of composites ranks from high to low as follows: Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/graphene composites obtained using CoSO\(_4\)-7H\(_2\)O as material, Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/graphene composites obtained using Co(NO\(_3\))\(_2\)-6H\(_2\)O as material, Co\(_3\)O\(_4\)/graphene composites. Among three composites, Co\(_3\)O\(_4\)/CoF\(_2\)-4H\(_2\)O/graphene composites prepared using CoSO\(_4\)-7H\(_2\)O as material exhibit high specific capacitance (241.8 F g\(^{-1}\) at 1 A g\(^{-1}\)), retention ratio of the specific capacitance (97.1% at the current density ranging from 1 to 4 A g\(^{-1}\)) and an excellent cycling stability (95.2% retention after 1000 cycles), indicating excellent rate
capability and cycling stability. These characteristics demonstrate that Co$_3$O$_4$/CoF$_2$·4H$_2$O/graphene composites prepared using CoSO$_4$·7H$_2$O as material possess a great potential application in supercapacitors.

ACKNOWLEDGEMENTS
This work was financially supported by Scientific Research Fund of Hunan Provincial Education Department (No. 14B022), Science and Technology Plan Fund of Changsha (No. k1509008-11) and Aid Program for Science and Technology Innovative Research Team in Higher Educational Institutions of Hunan Province.

References

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