Investigation of Enhanced Electrochemical Properties of Graphene/Fe₂O₃ Nanocomposite

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Graphite was used to prepare functionalized graphene oxide (GO) by Hummers method. The α-Fe₂O₃ powder was prepared by hydrothermal technique. Thin-film electrodes of GO, α-Fe₂O₃ (0.05. 0.1 and 0.2 M concentrations) and graphene coupled with α-Fe₂O₃@GO (1, 2 and 3 %) were prepared by spray pyrolysis technique using air and various optimized conditions: the distance between the spray nozzle and the substrate was 22 cm, the flow rate was 5 ml/min, and were used as anode material for supercapacitor. GO and α-Fe₂O₃@GO nanocomposite were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), and scanning electron microscopy (SEM). The FTIR showed the strong band at 1735 cm^{-1} associated with stretching vibration modes of C=O in carboxylic acid and carbonyl groups. The XRD (002) peak disappeared and the (111) peak appeared for graphite and GO, respectively, i.e., the product was completely oxidized after chemical oxidation and exfoliation. The SEM showed that thick sheets are stacked together. For electrochemical studies, cyclic voltammetry and stability of GO and α-Fe₂O₃@GO nanocomposite were carried out using three electrode configurations in 1 M KCl aqueous electrolyte. The GO, α-F$_{0.05}$, α-F$_{0.05}$@1%GO nanocomposites provided the maximum specific capacitance of 262, 201 and 312 F·g^{-1} at a scan rate of 2 mV·s^{-1}, respectively.

Keywords: Graphene, Fe₂O₃, Hummers method, Hydrothermal, Supercapacitor.

1. INTRODUCTION

The twenty-first century is the era of electronic gadgets, and every corner of the world is taking advantages of them. Hence, energy storage devices are required to operate electronic gadgets for better performance of green energy devices. Accordingly, a device, which delivers high power output, long service life and short charging time, is essential [1]. Therefore, the community needs energy storage devices that can quickly deal with crisis of fossil fuel [1]. Today supercapacitors are considered as a new class of energy storage devices that store energy with high specific capacitance. A supercapacitor mostly fills in the gaps between batteries and traditional capacitors. It is widely used in pulsed lasers, field-effect transistors, sensors, transparent conducting electrodes, field emitters [2, 3].

Now-a-days, carbon-based electrodes are used as anodes due to high specific surface area, excellent electrical conductivity and large power density [4]. To explore a new kind of anode electrode material, transition metal oxides such as Fe₃O₄, SnO₂ [5], NiO, Co₃O₄, V₂O₅, NiCOS₄ [6], Mn₃O₄ [7] are best suited due to multiple accessible valence states. Hence, to improve the supercapacitive performance [6], many transition metal oxides are combined with graphene material [3]. The redox reactions enhance the value of specific capacitance by 10-100 times depending on the nature of oxides [9]. Iron oxide has received considerable research attention due to its good intrinsic physical and chemical properties, such as low cost, stability under ambient conditions, and environmental friendliness [6, 7]. Published studies have confirmed that the use of a hematite-type Fe₂O₃ material with a conductive medium such as carbon tubes, carbon black graphene and polymers is an effective way to improve its electrochemical properties [6]. Li et al. [8] reported a specific capacitance of 214 F·g^{-1} at 1 A·g^{-1} for the solvothermal synthesis of Fe₂O₃-loaded activated carbon materials. Yang et al. [9] reported a specific capacitance of rod-like α-Fe₂O₃ meso-crystals/graphene nano-hybrids of 306.9 F·g^{-1} at 3 A·g^{-1} in an aqueous electrolyte.

In this research article, graphene oxide (GO) was synthesized by Hummers method and Fe₂O₃ powder was synthesized by one-step hydrothermal technique. Electrodes made of GO, Fe₂O₃ and Fe₂O₃/GO composites were fabricated by spray pyrolysis technique.

2. EXPERIMENTAL DETAILS

2.1 Synthesis of GO Powder

Graphene is synthesized by Hummers method from graphite powder as a source material [15, 16]. Initially, 1 g of graphite powder and 0.6 g of sodium nitrate were mixed together followed by the addition of concentrated sulfuric acid (H₂SO₄) with constant stirring in an ice bath at a temperature of 0 to 5 °C. To control the reaction temperature, potassium permanganate (KMnO₄) was gradually added to the solution to prevent overheating and explosion. The ice bath was then removed and stirred continuously until the mixture turned brownish. The resulting mixture was diluted by adding distilled water with stirring. The reaction temperature reached 98 °C with effervescence and color change to brown. To ensure the completion of the reaction with KMnO₄, the suspension was mixed with H₂O₂ solution. The resulting mixture was washed with HCl and H₂O, respectively, followed by vacuum filtration and drying; GO was obtained [10, 11].

2.2 Synthesis of GO Electrode

1 g of GO powder was mixed in ethylene glycol (EG). The solution was sprayed on a conducting substrate at a temperature of 200 °C at a rate of 3 ml/min [12].

2.3 Synthesis of a-Fe₂O₃ Powder

The a-Fe₂O₃ powder was synthesized using a hydrothermal route. Initially, 250 ml of a solution of Fe(NO₃)₃ with various concentrations (0.05, 0.1, 0.2 M), designated as a-F₀.₀₅, a-F₀.₁, a-F₀.₂, were prepared in distilled water with an appropriate amount. The resulting precursor suspension was transferred to a 250 ml Teflon-lined stainless-steel autoclave and filled with the reaction media to 80 %. The autoclave was kept in an oven at a maintained temperature of 200 °C for 4 h. After the reaction, the autoclave was naturally cooled to room temperature. The red solid precipitate was collected by centrifugation, washed with distilled water, and finally dried under vacuum.

2.4 Preparation of a- Fe₂O₃@GO Nanocomposite Electrodes

The initially synthesized GO and a-Fe₂O₃ (a-F₀.₀₅, a-F₀.₁ and a-F₀.₂) powder was mixed with EG under constant stirring and sprayed on stainless steel at 200 °C at a rate of 3 ml/min. These deposited electrodes were designated as a-F₀.₀₅@GO, a-F₀.₁@GO, a-F₀.₂@GO and were used for electrochemical studies.

3. RESULTS AND DISCUSSION

3.1 FTIR Analysis of GO

FTIR spectra (see Fig. 1) confirmed the presence of oxygen containing groups, such as functional hydroxyl, epoxy and carboxylic groups, after the oxidation of graphite powder [16]. The strong band at 1735 cm⁻¹ is associated with stretching vibration modes of C = O in carboxylic acid and carbonyl groups. The peak at 1616 cm⁻¹ corresponds to the stretching and bending vibrations of OH groups of water molecules adsorbed on graphene [12]. The stretching vibrations of alcohol C–OH group and O–H group are observed in absorption peaks at 1139 cm⁻¹ and 3347.43 cm⁻¹, respectively [12].
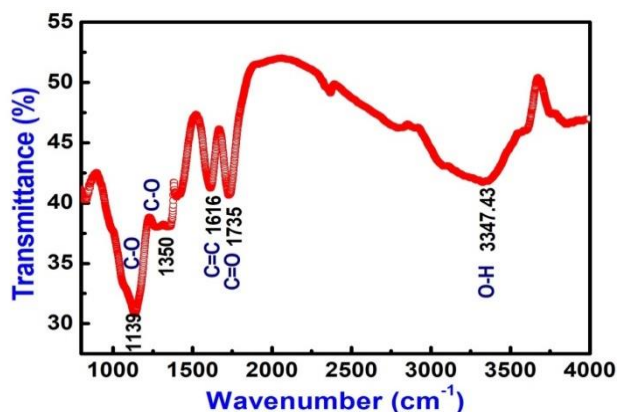

Fig. 1 – FTIR spectrum of GO powder

3.2 Structural Analysis

3.2.1 GO

X-ray diffraction (XRD) technique is used for crystalline material characterization. The XRD (002) peak of graphite (Fig. 2) was observed at $2\theta = 26.34°$, corresponding to the organized layer, and the GO (111) peak (the inset shows graphene) at $2\theta = 11.51°$, since the AB stacking order is still observed in graphene with an observed d-spacing of 0.75 nm [13]. This d-spacing is larger than the d-spacing (0.34 nm) of graphite. The XRD (002) peak disappeared and the (111) peak appeared for graphite and GO, respectively, indicating that the product was completely oxidized after chemical oxidation and exfoliation [10, 14].
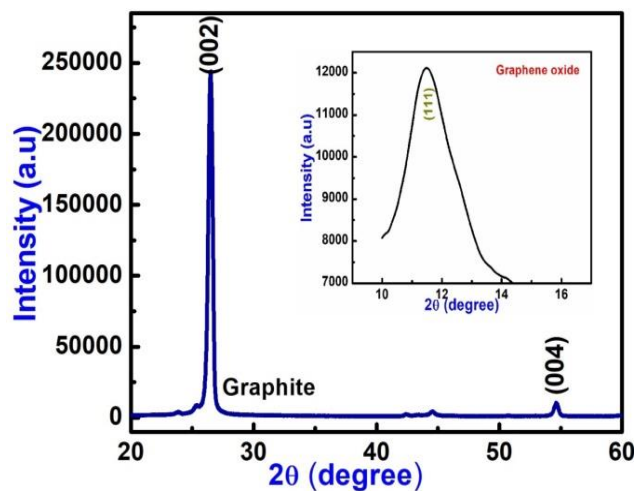

Fig. 2 – XRD pattern of graphene powder

3.2.2 a-Fe₂O₃@GO

Fig. 3 shows the XRD pattern of a-Fe₂O₃@GO (1, 2 and 3 %) in which all the peaks can be assigned to a-Fe₂O₃. Moreover, no conventional stacking peak (111) of graphite oxide at $2\theta = 11.51°$ is detected, suggesting that the graphene sheet can be individual monolayers that are homogeneously dispersed [15].
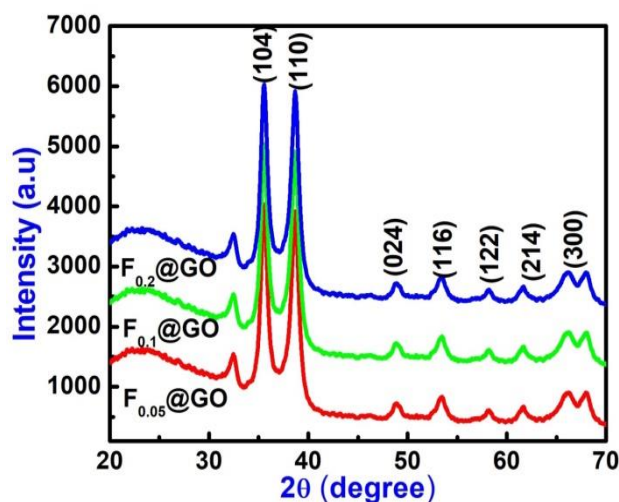

Fig. 3 – XRD pattern of a-Fe₂O₃@GO composites

3.3 Surface Morphological Studies

3.3.1 GO

Fig. 4 shows morphological images of as-prepared GO at different magnifications. Graphene shows that thick sheets are stacked together [15]. Rodbari et al. explained the similar surface morphology of GO, showing that oxidation of graphene causes changes in its morphology [16]. Fig. 7b shows that graphene sheets are exfoliated and arranged in pattern stacking [10].
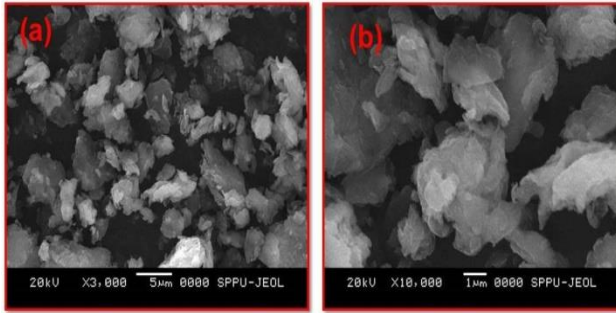

Fig. 4 – SEM micrographs of GO powder: (a) 5 µm, (b) 1 µm magnification

3.3.2 a-Fe$_2$O$_3$@GO

Fig. 5 shows the surface morphology of a-Fe$_2$O$_3$@GO (1, 2 and 3 %) composite electrodes with homogeneously distributed nanoparticles. It is observed that the nanoparticles have good adhesion and are moderately spread over the substrate surface. This type of surface morphology can be responsible for efficient energy storage applications, since it can provide better ion transfer between the electrode and the electrolyte solution [13].
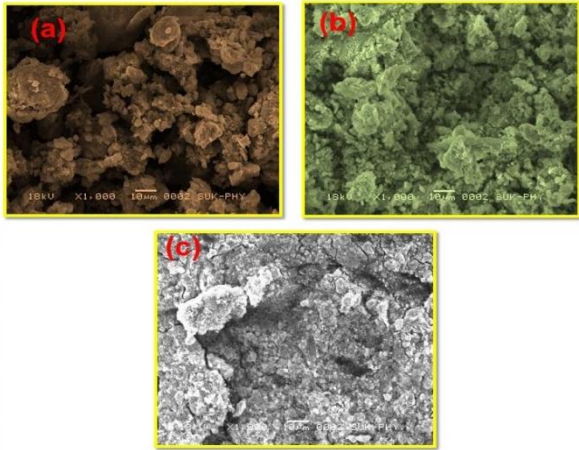

Fig. 5 – SEM micrographs of a-Fe$_2$O$_3$@GO composites: (a) 1 % GO, (b) 2 % GO, (c) 3 % GO

3.4 Electrochemical Measurement

3.4.1 Cyclic Voltammogram (CV) Analysis

3.4.1.1 GO

The CV profiles of the GO electrode obtained at different scan rates ranging from 2 to 100 mV·s^{-1} within a fixed potential window range of -1.2 to -0.3 V in aqueous 1 M KCl electrolyte are shown in Fig. 6. It is seen that the current increases with increasing scan rate, showing capacitive behavior [6]. Oxidation and reduction of the electrode material is confirmed by the redox reaction [18]. The specific capacitance of the GO electrode is determined using the following equation [19]:

$$SC = 1 \times \int \frac{Idv}{m \times \Delta V \times s}, \qquad (1)$$

where I is the current of the sample per unit area (1 cm^2), m is the mass of an active electrode with 1 cm^2 surface area deposited on a stainless steel substrate, ΔV is the potential window, and s is the sweep rate.
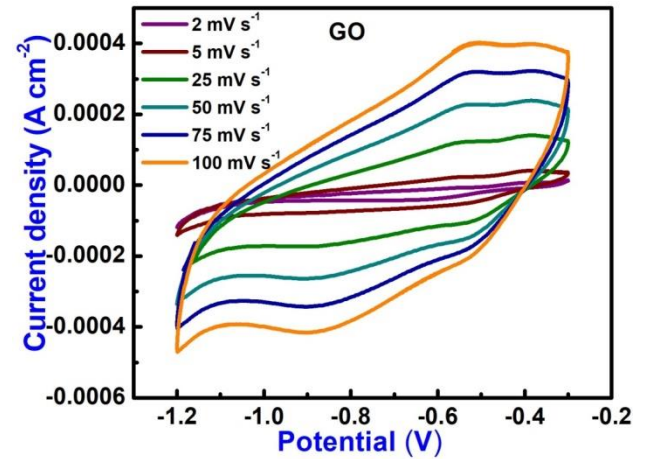

Fig. 6 – CV curves of the thin-film GO electrode at different scan rates in 1 M KCl electrolyte

The specific capacitance values of the GO electrode were found to be 262, 197, 141, 113, 98 and 92 F·g^{-1} at scan rates of 2, 5, 25, 50, 75, 100 mV·s^{-1}, respectively. It is found that the specific capacitance is inversely proportional to the scan rate. At low scan rates, diffusion of K$^+$ ions can reach available active sites due to absorption in the GO electrode [6, 20]. At higher scan rates, K$^+$ ions can restrict active sites. As a result, they cannot use the inner surface. Therefore, a complete redox transition may not complete at higher scan rates, which contribute to the capacitance values [10, 18].

The calculated values of the specific capacitance, energy density, and power density of the GO film electrode are summarized in Table 1.

The electrochemical performance such as energy density (E), power density (P) and efficiency was calculated using the following equations [19]:

$$E = \frac{V \times Id \times td}{m}, \qquad (2)$$

$$P = \frac{V \times Id}{m}, \qquad (3)$$

where I_d is the discharge current, t_d is the discharge time, t_c is the charge time, V is the voltage, and m is the mass,
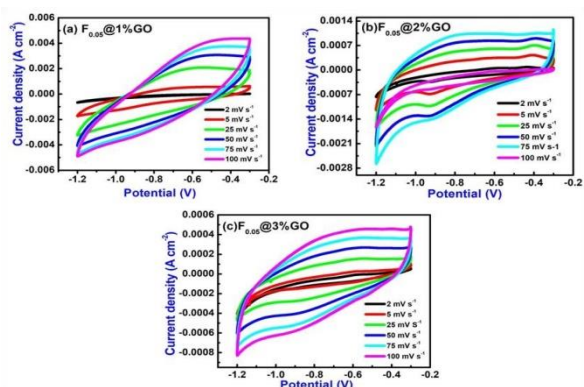
$$\eta = \frac{\Delta td}{\Delta tc}, \qquad (4)$$

where Δt_d and Δt_c represent discharge and charge times, respectively.

The calculated values of the specific capacitance, energy density, power density, and efficiency of α-Fe$_2$O$_3$ electrode are summarized in Table 1.

3.4.1.2 α-Fe$_2$O$_3$@GO

To realize the potential relevance of α-F$_{0.05}$@GO (1, 2 and 3 %) for supercapacitor applications, the balance of the mass ratio of α-Fe$_2$O$_3$@GO in the composite is important [28]. In the present study, we synthesized α-F$_{0.05}$@GO hybrid electrode with 1, 2 and 3 % graphene powder mixed with α-F$_{0.05}$ electrode. The CV curves of α-F$_{0.05}$@GO with composite electrodes (1, 2, 3 % GO) are shown in Fig. 7. The hybrid electrode α-F$_{0.05}$@1%GO showed the best electrochemical performance. The ma-
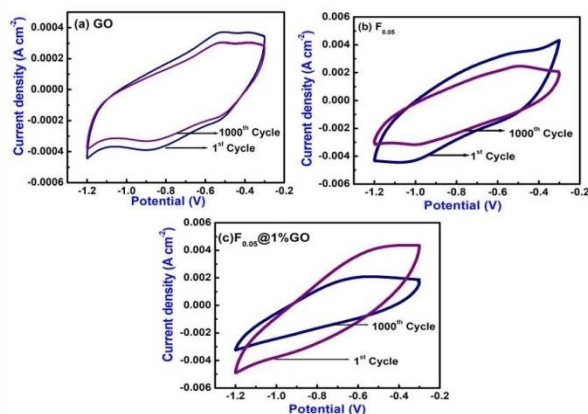
ximum specific capacitance of 312 F·g^{-1} was shown by α-F$_{0.05}$@1%GO. The calculated values of the specific capacitance, energy density, power density and efficiency of α-Fe$_2$O$_3$@1%GO film electrode are summarized in Table 1.

3.4.2 Stability of GO, α-F$_{0.05}$ and α-F$_{0.05}$@1%GO

The most essential factor in energy storage is the long-term cyclic stability of the electrode [6, 19]. The long-term cyclic stability and reversibility of porous GO, α-F$_{0.05}$ and α-F$_{0.05}$@1%GO electrodes were evaluated by repeating the CV test in the range of -1.2 to -0.3 V at a scan rate of 100 mV·s^{-1}; the results are shown in Fig. 8. Furthermore, there is no change in the CV curve before and after 1000th cycles.

Fig. 7 – CV curves of α-Fe$_2$O$_3$@GO: (a) 1 % GO, (b) 2 % GO and (c) 3 % GO thin films at different scan rates in 1 M KCl electrolyte

Fig. 8 – Stability study of (a) GO, (b) α-F$_{0.05}$, (c) α-F$_{0.05}$@1%GO

Table 1 – Specific capacitance, energy, power density and efficiency values of GO, α-Fe$_2$O$_3$ and α-Fe$_2$O$_3$@GO film electrodes in 1 M KCl electrolyte

Electrode	Specific capacitance, F·g^{-1}		Specific energy, Wh·kg^{-1}	Specific power, kW·kg^{-1}	Coulomb efficiency, %
	CV	CP			
GO	262	248	32.18	47.90	90
F$_{0.05}$	201	158	11.66	11.55	59.46
F$_{0.1}$	152				
F$_{0.2}$	248				
F$_{0.05}$@1%GO	312	291	20.47	19.39	81
F$_{0.05}$@2%GO	229				
F$_{0.05}$@3%GO	157				

4. CONCLUSIONS

GO was successfully synthesized by Hummers method from graphite powder. A simple spray pyrolysis method was employed to prepare a high-quality GO electrode. The XRD (002) peak of graphite observed at $2\theta = 26.34°$ corresponds to a highly organized layered structure and GO at 2θ of 11.51°, which is mainly due to the oxidation of graphite. FTIR of GO confirmed the existence of oxygen functional groups and the presence of C–O and C=C bonds. SEM showed exfoliation of graphene. Electrochemical study was carried at differ-

ent scan rates within a fixed potential window range of -1.2 to -0.3 V in aqueous 1 M KCl electrolyte. The maximum specific capacitance of GO, α-F$_{0.05}$ and α-F$_{0.05}$@1%GO electrodes from CV and charge/discharge curves were found to be 262, 201, 312 F·g^{-1} and 248, 158 and 291 F·g^{-1}, respectively.

REFERENCES

1. D.P. Dubal, P.G. Romero, Chem. Soc. Rev. 47, 2065 (2018).
2. U.M. Patil, R.R. Salunkhe, K.V. Gurav, C.D. Lokhande, *Appl. Surface Sci.* **255**, 2603 (2008).
3. H.Y. Koo, H.J. Lee, H.A. Go, Y.B. Lee, T.S. Bae, J.K. Kim, W.S. Choi, *Chem – A Euro. J.* **17**, 1214 (2011).
4. H. Wanga, Z. Xua, H. Yi, H. Wei, Z. Guob, X. Wang, *Nano Energy* **7**, 86 (2014).
5. M. Jayalakshm, K. Balasubramanian, *Inter. J. Electrochem. Sci.* **3**, 1196 (2008).
6. X. Zheng, X. Yan, Y. Sun, Y. Yu, G. Zhang, Y. Shen, Q. Liang, Q. Liao, Y. Zhang, *J. Collide Inter. Sci.* **466**, 291 (2016).
7. P.D. More, P.R. Jadhav, S.M. Ingole, Y.H. Navale, V.B. Patil, *J. Mater. Sci. Mater. Elect.* **28**, 707 (2017).
8. L.K.Y. Li, G.L. Bai, P.Y. Li, J.C. Deng, X.G. Liu, F.G. Yang, W. Liang, *Electrochim.* **134**, 67 (2014).
9. S. Yang, X. Song, P. Zhang, J. Sun, L. Gao, *Small* **10**, 2270 (2014).
10. B. Paulchamy, G. Arthi, B.D. Lignesh, *J. Nanomed. Nano-tech.* **6**, 1 (2015).
11. L. Shahriary, A.A. Athawale, *Inter. J. Renew. Ener. Envir. Eng.* **2**, 58 (2014).
12. M.S. Eluyemi, M.A. Eleruja, A.V. Adedeji, B. Olofinjana, O. Fasakin, O.O. Akinwunmi, O.O. llori, A.T. Famojuro, S.A. Ayinde, E.O.B. Ajayi, *Graphene* **5**, 143 (2016).
13. I.T. Kim, A. Magasinski, K. Jacob, G. Yushin, R. Tannenbaum, *Carbon* **52**, 56 (2015).
14. S. Chen, J. Zhu, X. Wu, Q. Han, X. Wang, *ASC Nano.* **4**, 2822 (2010).
15. T. Han, Y. Wei, X. Jin, H. Jiu, L. Zhang, Y. Sun, J. Tian, R. Shang, D. Hang, R. Zhao, *J. Mater. Sci.* **54**, 7119 (2019).
16. R.J. Rodbari, R. Wendelbo, L.C.L.A. Jamshidi, E.P. Hernandez, L. Nascimento, *J. Chil. Chem. Soc.* **61**, 3120 (2016).
17. H.J. Choi, S.M. Jung, J.M. Seo, D.W. Chang, L. Dai, J.B. Baek, *Nano Energy* **1**, 534 (2012).
18. L.X. Liang, X. Yan, W. Hua, W.H. Lin, C.X. Ying, *Trans. Nonferrous Met. Soc.* **19**, 620 (2009).
19. P.D. More, P.R. Jadhav, A.A. Ghanwat, I.A. Dhole, Y.H. Navale, V.B. Patil, *J. Mater. Sci.: Mater. Elect.* **28**, 17839 (2017).
20. T. Han, Y. Wei, X. Jin. H. Jiu, L. Zhang, Y. Sun, J. Tian, R. Shang, D. Hang, R. Zhao, *J. Mater. Sci.* **54**, 7119 (2019).

Дослідження покращених електрохімічних властивостей нанокомпозиту графен/Fe₂O₃

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Графіт використовували для приготування функціоналізованого оксиду графену (GO) методом Хаммерса. Порошок α-Fe₂O₃ отримували гідротермальною технікою. Тонкоплівкові електроди з GO, α-Fe₂O₃ (концентрації 0,05; 0,1 та 0,2 M) і графену у поєднанні з α-Fe₂O₃@GO (1, 2 та 3 %) були підготовлені методом спрей-піролізу за допомогою повітря та різних оптимізованих умов: відстань між розпилювачем та підкладкою становила 22 см, швидкість потоку була 5 мл/хв, і вони використовувалися як анодний матеріал для суперконденсатора. GO та нанокомпозит α-Fe₂O₃@GO характеризувалися інфрачервоною спектроскопією з перетворенням Фур'є (FTIR), порошковою рентгенівською дифракцією (XRD) та скануючою електронною мікроскопією (SEM). Дослідження FTIR показали, що смуга з підвищеною пропускною здатністю при 1735 см⁻¹ пов'язана з модами валентних коливань C=O в карбонових кислотах та карбонільних групах. XRD пік (002) зник, а пік (111) з'явився для графіту та GO відповідно, тобто вихідний продукт повністю окислився після хімічного окислення та відшарування. Результати SEM показали, що товсті графенові поверхні складені разом. Що стосується електрохімічних досліджень, циклічну вольтамперометрію та стабільність GO та нанокомпозиту α-Fe₂O₃@GO проводили з використанням трьох конфігурацій електродів у 1 M водному електроліті KCl. GO та нанокомпозити α-F₀.₀₅, α-F₀.₀₅@1%GO забезпечували максимальну питому ємність відповідно 262, 201 і 312 Ф·г⁻¹ при швидкості сканування 2 мВ·с⁻¹.

Ключові слова: Графен, Fe₂O₃, Метод Хаммерса, Гідротермальний, Суперконденсатор.