NiO-Co$_3$O$_4$-rGO as an Efficient Electrode Material for Supercapacitors and Direct Alcoholic Fuel Cells

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Transition metal oxides can be performant electrode materials for supercapacitors and alcohol oxidation if their conductivity and capacity are improved. Herein, an advanced nanocomposite material made of NiO-Co$_3$O$_4$ on reduced graphene oxide (rGO) is synthesized by a one-step hydrothermal method for supercapacitors and methanol/ethanol oxidation. It is demonstrated that the nanocomposite is a promising material for energy storage as NiO-Co$_3$O$_4$-rGO supercapacitor electrodes achieve a specific capacity of 149 mAh g$^{-1}$ (894 F g$^{-1}$) at a current density of 0.5 A g$^{-1}$, the discharge time of 689 s, and excellent stability of 95% after 6000 cycles. Moreover, NiO-Co$_3$O$_4$-rGO shows a current density of 15 and 10 mA cm$^{-2}$ in methanol and ethanol oxidation reactions, respectively, along with excellent stability.

1. Introduction

In the present century, the usage of renewable energy sources and clean fuels has been very important.[1] In this context, solar cells, wind turbines, and geothermal energy have been considered suitable solutions to overcome the lack of energy and global warming due to fossil fuel consumption. In recent years, boosted by the extensive progress in the field of nanoscience, energy storage devices have attracted great attention by the researchers around the world. Among these devices, we can mention fuel cells, supercapacitors, and batteries.[2]

On the subject of energy storage, supercapacitors have a particular role due to the low price of their electrode materials as well as their wide application in various industries.[3,4] The charge storage mechanism of the electroactive materials can be identified as electrical double-layered capacitance (EDLC), pseudo-capacitance (PCS), and battery-type behavior.

EDLCs do not show any oxidation peak in cyclic voltammetry (CV) and just indicate capacitive (non-faradic) current. PCSs are between EDLCs and batteries in terms of charge storage mechanism, in which the surface Faradaic electron transfer to metal centers occurs by the intercalation or adsorption of charge-compensating ions.[5] They are including underpotentinal deposition, (surface or near-surface) redox pseudo-capacitance, and intercalation pseudo-capacitance.[6–8]

Electrode materials that show EDLC behavior include carbonaceous materials,[9] a large number of metal-organic frameworks (MOFs),[10] and conductive polymers.[11] Conversely, 2D nanomaterials such as transition metal oxides/sulfides have pseudocapacitance or battery behavior.[12–16] Transition metal oxides are very attractive due to their good chemical and mechanical stability, and the high capability in the field of supercapacitors predicted by theoretical calculations. However, the poor conductivity and p-type behavior is an important disadvantage of metal oxides to overcome.[17,18] Yet, many studies have been performed on supercapacitor effects of transition metal oxides such as RuO$_2$, NiO, and MnO$_2$.[19,20]

In the field of clean energies, various types of fuel cells especially direct alcoholic fuel cells (DAFC), direct methanol fuel cells (DMFC), and direct ethanol fuel cells (DEFC) are taken into consideration due to their low operating temperature and relatively significant efficiency. Among alcoholic fuel cells, direct methanol and ethanol fuel cells are considered more than other fuel cells due to some advantages such as high theoretical energy density and low cost. However, the sluggish kinetics of alcohol oxidation is still a challenge. This is mostly due to poisoning of the surface of the electrocatalyst material by adsorbed CO, which leads to an efficiency drop in the DAFC. One of the strategies to overcome this problem is preparing co-catalyst

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materials that can provide OH species at lower potentials for adsorption of the CO.[21]

Although Pt-based materials have been widely used in DAFCs, some disadvantages such as high cost and low reaction kinetics for alcohol electrooxidation have limited the widespread use of these catalysts.[22] Conversely, transition metal oxides as economical materials can play the role of both the support and the catalyst/co-catalyst for electrode materials in alcohol electrooxidation. The oxygenated species can handle the alcohol oxidation and the reaction between intermediates in the alkaline setting.[23] On the other hand, in multicomponent catalysts, the energy gap between HOMO and LUMO decreases. As a result, the charge transfer between the substrates accelerates by the synergetic effect.[24,25]

Recently, several strategies have been considered for the development of transition metal oxides catalysts for DMFC and DEFC. One strategy is combining metal oxides with conductive carbon materials to enhance electrical conductivity and increase active sites.[26,27] Another strategy is to make a catalyst using hybridization of active materials, that is, to combine different metal oxides to take advantage of both components simultaneously through a synergistic effect and to reinforce each other, thus increasing electrocatalytic performance. Some combined metal oxides have been reported in the literature such as CeO2−NiO,[28] Cu-Ni/CuO-NiO,[29] CuO/TiO2/Pd-NiO,[30] and Co3O4/NiO,[31] which have shown improved electrochemical performance for DMFC and DEFC.

Based on the above two strategies, in the present study, NiO-Co3O4/rGO multicomponent nanocomposite material is synthesized by a simple hydrothermal method for supercapacitors and methanol/ethanol oxidation. RGO is exploited to increase the active surface area and conductivity of the electrode material. The electrochemical properties of the as-prepared nanocatalyst are evaluated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), galvanostatic charge/discharge (GCD), and linear sweep voltammetry (LSV). Overall, the synergistic effects between the two NiO and Co3O4 metal oxides along with the hybridization with rGO lead to high specific capacity and long discharge time in the field of supercapacitor. Moreover, the synthetic nanocatalyst shows a high current density with a reduced overvoltage for methanol (MOR) and ethanol (EOR) oxidation processes, thus constituting an effective, low-cost, easy-to-prepare, and stable bifunctional electrocatalyst.

2. Results and Discussion

2.1. Characterization of the Synthetic Material

To study the crystalline structure and particle size of the as-prepared materials, the XRD technique was performed as shown in Figure 1. The reduced graphene oxide shows two wide peaks in the diffraction pattern. Also, Figure 1 represents the XRD pattern of the NC nanocomposite. As can be seen, the diffraction peaks of NiO for (111), (220), (311), (222), (400), (511), (440), and (333) planes were detected at 2θs of 19.0°, 31.5°, 36.9°, 39.0°, 45.0°, 59.5°, 65.5°, and 78.0°, respectively, which confirmed full compliance with JCPDS card no of 047-1049.[32] Besides, diffraction peaks for (111), (220), (220), (311), and (222) observed at 2θs of 37.1°, 43.3°, 63.0°, 75.5°, and 79.5°, respectively, which are in agreement with Co3O4 pattern through JCPDS card no 01-080-1532.[33] The crystal size of the prepared material, using the Scherer equation \(D = \beta \cos \theta/\lambda\),[34] obtain about 20 nm. In the diffraction pattern of NCR, the distribution of NC on the graphene surface reduces its crystalline structure that causes a decrease in peak intensity.

To study the surface morphology of the synthetic nanomaterials, SEM images of NC and NCR were taken. Figure 2a,b shows SEM images of NC in two scales of 200 and 500 nm. Also, in Figure 2c–d, SEM images of NCR are shown in the same scales and confirm the presence of graphene nanosheets and the uniform distribution of NC. Figure 2e shows the SEM image of graphene nanoplates. Elemental EDX mapping analysis was obtained to prove the uniform placement of NC nanoparticles on the surface of graphene nanosheets. As well, Figure 2f shows the uniform dispersion of NC on the graphene surface and proves the presence of nickel, cobalt, oxygen, and carbon elements in the structure of the as-prepared nanocomposite.

TEM micrographs of NC and NCR are shown in Figure 3a,b. NC has an average particle size of 35 nm, which agrees with XRD results. The particle size distribution histogram of NC is shown in the inset of Figure 3a. 100 nanoparticles were considered to measure the size distribution histogram. NC nanoparticles are in the narrow range of 20–50 nm. The peak of about 35 nm defines the average size of nanoparticles. Besides, the uniform dispersion of NC on the surface of transparent sheets of rGO is clear in Figure 3b.

2.2. Electrochemical Studies

2.2.1. Investigation of Materials as Supercapacitor Electrode

To investigate the supercapacitor properties of NC and NCR nanomaterials, a 2 M solution of KOH was prepared as the electrolyte and electrochemical tests, namely CV, charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed at the mentioned alkaline electrolyte. The charge transfer mechanism of the two proposed electrodes was checked...
by cyclic voltammetry test at different potential scan rates. Figure 4a–c shows the behavior of rGO, NC, and NCR electrodes in 2 \text{m} of KOH electrolyte at different potential scan rates over the range 0–0.6 V, respectively. Figure 4a represents the capacitive behavior of rGO. With increasing scan rate, the CV curve is broadened, and the current density is enhanced. The shape of CV curves is fixed and symmetric at all scan rates, confirming a high-rate performance and desirable capacitive behavior. Figure 4b shows a faradic red/ox process for NC electrode through cyclic voltammetry. Besides, the addition of rGO to the NC structure led to an increase in current density and broadening of red/ox peaks compared to NC (Figure 4c). The redox peaks in each cycle reveal that the specific capacity is mostly due to the reversible faradaic reactions. In Figure 4c, in the CV curves of NCR, the oxidized area is nearly equal with the reduced area, which suggests materials that get oxidized are reduced back. Besides, with increasing potential scan rate, the peak current is increasing. These results indicate the serious role of electrochemical polarization. The electrochemical reactions on NC are the following:\(^{(1)}\)

\[
\text{NiO} + \text{OH}^- \leftrightarrow \text{NiOOH} + e^- \\
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow 3\text{CoOOH} + e^- \\
\text{CoOOH} + \text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^- 
\]

Figure 2. SEM images of a,b) NC, c,d) NCR in scales of 200 and 500 nm, e) rGO, and f) elemental EDX mapping of NCR.
By examining the behavior of the electrodes at various scan rates (10–100 mV s\(^{-1}\)), it can be found that the specific capacity is inversely related to the potential scan rate. In Figure 4d, the specific capacity is plotted versus various scan rates. From the diagram, it is clear that the addition of rGO to the NC enhances the specific capacity of the electrode resulting
from the synergic effect between metal oxides and rGO. Metal oxides have good theoretical potential in energy storage and rGO increases the conductivity and surface area of electrode materials. Thus, the synergistic effect between NC and rGO makes an efficient electrode for energy storage. Besides, NC and rGO supply energy storage through redox pseudocapacitance and EDLC mechanism, respectively. At the low scan rate of 10 mV s⁻¹, the highest specific capacity was observed because, at the lower scan rates, the electrolyte ions have enough opportunity to penetrate the electrode. At high scan rates, the hydroxide ions have a shorter time and only access the outer active sites. The values of specific capacity for NCR are 181, 165, 153, 145, 140, and 138 mAh g⁻¹ at the scan rates of 10, 20, 40, 60, 80, and 100 mV s⁻¹, respectively, while the maximum specific capacity for NC is 110 mAh g⁻¹. Figure 4e shows the plot of the current density against the square root of scan rate for both the NC and NCR electrodes. The linearity of plots indicates that the electrochemical reactions occur on the electrode surface during a diffusion-controlled process.

The specific capacity was calculated by using the following equation from CV curves:

\[ C = \frac{1}{2m\nu} \int I \, dV \]  

(4)

while the specific capacitance was obtained as:

\[ C' = \frac{1}{2m\Delta V} \int I \, dV \]  

(5)

where, \( m \) is mass loading of sample on carbon cloth, \( \nu \) is scan rate, \( \Delta V \) is potential window, \( \int I \, dV \) is the integrated area under the CV curve. Figure 4f represents the EIS analysis for the NC and NCR electrodes. In this diagram, the charge transfer resistance (\( R_{ct} \)) can be obtained by measuring the diameter of the semicircles. The values of \( R_{ct} \) for NC and NCR electrodes were calculated 6.55 and 3.5 Ω, respectively, indicating the efficient role of rGO in increasing conductivity. The comparison of the Warburg lines of the electrodes also confirms the facilitation of ion diffusion in the NCR electrode compared to NC, which proves the increase in surface area and active sites by the addition of rGO to the catalyst structure.

GCD analysis was performed to study the ability of NC and NCR electrodes for electrical charge storage at the current densities of 0.5, 1, 2, and 4 A g⁻¹. Figure 5a,b shows the GCD diagrams of the NC and NCR electrodes. The charge storage process in two electrodes resulted from capacitive and Faradic behavior. The GCD curves of the two electrodes are not symmetric and linear, indicating that redox reactions have the main contribution in the specific capacity. Electrochemical reactions related to the charge storage caused by red/ox reactions as \( \text{Ni}^{2+}/\text{Ni}^{4+} \), \( \text{Co}^{2+}/\text{Co}^{3+} \), and \( \text{Co}^{3+}/\text{Co}^{4+} \). The highest discharge rate, as well as the highest specific capacity, is seen at the lowest current density (0.5 A g⁻¹).

In the NCR electrode, the synergistic effect between \( \text{NiO}, \text{Co}_3\text{O}_4 \), and rGO led to a highly conductive and active electrode. It also causes the NCR electrode to have a longer discharge time and higher specific capacity (149 mAh g⁻¹, capacitance of 894 F g⁻¹) at a current density of 0.5 A g⁻¹ than

Figure 5. GCD curves of a) NC and b) NCR at different current densities, c) cycling performance of NCR 6000 consecutive cycles, d) cycling performance of NCR at 0.5 A g⁻¹ in 1000 GCD cycles (Inset shows GCD test before and after cyclic stability test).
NC (101 mAh g\textsuperscript{−1}). In Table 1, the specific capacity and the specific capacitance at different current densities for two electrodes were calculated using the following equations from GCD curves:\textsuperscript{[37]}

$$C = \frac{I \Delta t}{m}$$ \quad (6)

and

$$C' = \frac{I \Delta t}{m \Delta V}$$ \quad (7)

where I is the current density, \(\Delta t\) is the discharge time, m is the mass loading, and \(\Delta V\) is the potential window.

To evaluate the stability of the NCR electrode, 6000 consecutive cycles were performed at the scan rate of 10 mV s\textsuperscript{−1}. Figure 5c shows the first and 6000th cycle. After the applied cycles, just a 5% decrease in specific capacity was observed. Also, the stability of the electrode using GCD was examined with 1000 repeated charge/discharge at the current density of 0.5 A g\textsuperscript{−1} cycles that showed no change in the shape of the discharge/charge curves (Figure 5d). Besides, the discharge time is not significantly reduced during 1000 cycles and the capacity retention obtains 91%. The inset of Figure 5d shows GCD curves of NCR before and before the stability test indicates a negligible change in discharge time. This result is in agreement with CV results (Figure 5c).

A comparison of the electrochemical properties of our material with some metal oxides is shown in Table 2. The specific capacity and cyclic stability of NCR are comparable with other works.

### 2.2.2. Investigation of the Methanol Oxidation Process

To study the electrochemical behavior of NC and NCR nanocatalysts in the methanol oxidation process, cyclic voltammetry tests were performed at the scan rate of 60 mV s\textsuperscript{−1} in 2 M KOH and 1 M methanol. Figure 6a shows that both catalysts respond to methanol oxidation by originating the related oxidation peaks. However, the position of the peaks and the current densities were different. The methanol oxidation peak for NCR appears at lower overvoltage and peak potential and shows higher current density due to its higher conductivity and more active surface area. The comparison of the CV curves of two electrodes in the MOR process confirmed the effective role of rGO in the hybrid, by reducing peak potential from 0.63 to 0.60 V and increasing current density from 0.9 to 15 mA cm\textsuperscript{−2}.

A six-electron mechanism of the NCR nanocatalyst for the MOR process is proposed as follows.

$$\text{NCR} + \text{CH}_3\text{OH} \rightarrow \text{NCR} - \text{CH}_3\text{O}H_{\text{ads}}$$ \quad (8)

$$\text{NCR} - \text{CH}_3\text{O}H_{\text{ads}} + 4\text{OH}^- \rightarrow \text{NCR} - (\text{CO})_{\text{ads}} + 4\text{H}_2\text{O} + 4e^-$$ \quad (9)

$$\text{NCR} + \text{OH}^- \rightarrow \text{NCR} - \text{OH}_{\text{ads}} + e^-$$ \quad (10)

### Table 2. Comparison of electrochemical properties of some metal oxides.

| Electrode material | Support material | Electrolyte | C [F g\textsuperscript{−1}] | Stability-cycle number | Ref. |
|--------------------|-----------------|-------------|-----------------|------------------------|-----|
| 3D ZnO/rGO        | CVD             | 6 M KOH     | 275             | 62%–1000               | [38]|
| Ni-Co-S@N-pCNFs   | Ni-foam         | 3 M KOH     | 670             | 90%–3000               | [39]|
| Ni-Co-S/graphene  | Ni-foam         | 6 M KOH     | 178.1           | 89.47%–10 000          | [40]|
| FeO\textsubscript{2}O\textsubscript{2}@MoS\textsubscript{2}/rGO | CVD | 6 M KOH | 527 | 93%–5000 | [41]|
| Cu\textsubscript{2}O/CuO/Co\textsubscript{3}O\textsubscript{4} | Ni-foam | 3 M KOH | 318 | 80%–3000 | [42]|
| RGO-Co\textsubscript{3}O\textsubscript{4}/Py | Ni-foam | 6 M KOH | 532.8 | 81%–5000 | [43]|
| NiO/rGO           | Ni-foam         | 6 M KOH     | 171.3           | 79.07%–2000            | [44]|
| CuO/NiO/N-rGO     | Ni-foam         | 5 M KOH     | 220             | 97%–5000               | [45]|
| Co\textsubscript{3}O\textsubscript{4}@N-rGO | Ni-foam | 2 M KOH | 450 | 99%–2000 | [46]|
| NiFe\textsubscript{2}O\textsubscript{3}/rGO | CVD | 2 M KOH | 584.63 | 91%–2000 | [2]|
| NiO@Co\textsubscript{3}O\textsubscript{4} | Carbon cloth | 6 M KOH | 348.45 | 92.6%–5000 | [47]|
| NIO-Co\textsubscript{3}O\textsubscript{4} | Graphene foam | 2 M KOH | 766 | 86%–5000 | [48]|
| NiO@Co\textsubscript{3}O\textsubscript{4} nanofibers | Ni-foam | 6 M KOH | 788 | 93%–10 000 | [49]|
| CoAl-LDH/graphene oxide | Ni-foam | 6 M KOH | 722 | 73%–10 000 | [50]|
| Co-doped Ni(OH)\textsubscript{2} | CVD | 1 M KOH | 1421 | 76%–1000 | [41]|
| Co-Ni layered double hydroxides (LDHs) | Ni-foam | 3 M KOH | 2275 | 80%–1800 | [51]|
| NCR                | Carbon cloth    | 2 M KOH     | 894             | 95%–6000 CV            | This work |

This work indicates a negligible change in discharge time. This result is in agreement with CV results (Figure 5c).
The stability of NCR and NC nanocatalysts was also investigated in the MOR process during 2000 continuous cycles. Comparing the plots of Figure 6b,c, it can be concluded that both nanocatalysts possess considerable stability in the MOR process. NC and NCR catalysts represent the stability of 95% and 97%, respectively. The reason for the greater stability of NCR may be due to the higher active sites and greater conductivity.

The effect of temperature in the methanol oxidation process was studied by applying linear sweep voltammetry (LSV) test at the scan rate of 60 mV s⁻¹. Figure 6d shows that the methanol adsorption process on the catalyst surface is facilitated by increasing the temperature from 290 to 310 K. The linear relationship between the temperature and current density is shown in Figure 6d. The increasing current density with raising temperature indicates an improvement in the MOR process.

### 2.2.3. Investigation of the Ethanol Oxidation Process

The direct ethanol fuel cell (DEFC) can be important due to greenness. Here, the potential of the two nanocatalysts, NC and NCR, in the process of ethanol oxidation was studied in alkaline media containing 2 m of KOH at the presence of 1 m of ethanol at the scan rate of 60 mV s⁻¹. Although a higher peak potential and a lower current density were observed compared to the MOR process, catalyst capability in ethanol oxidation can be considered in the current research. The comparison of cyclic voltammetric analysis between NC and NCR was shown in Figure 7a. The oxidation peak of the catalyst hybridized with rGO appears in lower potential (0.6 V) and higher current density (10 mA cm⁻²) relative to NC (0.7 V and 8 mA cm⁻²). It is believed that rGO can facilitate the ethanol oxidation process by increasing the active surface area and conductivity. The suggested mechanism of ethanol oxidation in alkaline media is proposed as follows.⁵²

\[
\text{NCR} + \text{OH}^{\cdot} \rightarrow \text{NCR} - \text{OH}_{\text{ads}} + e^{-} \tag{12}
\]

\[
\text{NCR} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{NCR} - (\text{CH}_3\text{CH}_2\text{OH})_{\text{ads}} \tag{13}
\]

\[
\text{NCR} - (\text{CH}_3\text{CH}_2\text{OH})_{\text{ads}} + 3\text{OH}^{\cdot} \rightarrow \text{NCR} - (\text{CH}_3\text{CO})_{\text{ads}} + 3\text{H}_2\text{O} + 3e^{-} \tag{14}
\]

\[
\text{NCR} - (\text{CH}_3\text{CO})_{\text{ads}} + \text{NCR} - \text{OH}_{\text{ads}} \rightarrow \text{NCR} - (\text{CH}_3\text{COOH})_{\text{ads}} + \text{NCR} \tag{15}
\]

\[
\text{NCR} - (\text{CH}_3\text{COOH})_{\text{ads}} + \text{OH}^{\cdot} \rightarrow \text{NCR} + \text{CH}_3\text{COO}^{\cdot} + \text{H}_2\text{O} \tag{16}
\]

The stability of NC nanocatalyst after 2000 cycles was 88% and for the nanocatalysts hybridized with EOR was calculated about 92% (Figure 7b,c). To investigate the effect of temperature in the EOR process, the linear sweep voltammetry test was performed at the scan rate of 60 mV s⁻¹ and temperatures of 290, 295, 300, and 310 K. Figure 7d shows that ethanol oxidation is facilitated by increasing the temperature due to effective
adsorption of ethanol molecules on the surface of the catalyst. The linear relationship between temperature and current density is also shown in the inset of Figure 7d.

The chronoamperometry was conducted in the electrolyte solutions containing 1 m methanol/2 m KOH and 1 m ethanol/2 m KOH at the anodic peak potential (0.62 V for MOR and 0.70 V for EOR), as shown in Figure 8. At the initial times, the current density is dropped quickly because of the presence of carbonaceous intermediate species on the surface of the catalyst. After that, in longer times the current density reached a rather stable value, about 11 mA cm\(^{-2}\) for NCR (73% stability) in MOR and 6.5 mA cm\(^{-2}\) for NCR (65% stability) in EOR. The stability of NCR results from good dispersion of NC and conductivity of rGO.

The electrochemical properties of the as-prepared materials with some metal oxides for alcohol oxidation are compared in Table 3. Although the current density of NCR is lower than that of other reported materials, the peak potential is comparable with other works. It is noted that the current collector and loading of catalyst on its surface are important factors that should be considered.

3. Conclusion

Briefly, a nanocomposite containing two transition metal oxides, NiO and Co\(_3\)O\(_4\), was synthesized by a simple hydrothermal method as material for supercapacitors and DAFC.
According to the previous work, NiO-Co₃O₄ (NC) was prepared (Metrohm). Tests were also performed with galvanostat/potentiostat PGSTAT302N. TEM images were obtained using a Philips EM 2085. Electrochemical studies were studied by scanning electron microscopy (SEM) through Hitachi PANalytical and also the morphology of the synthetic nanomaterials was prepared from Merck. A solution of 5% Nafion was prepared from Sigma Aldrich. Other needed chemicals were used in their analytical grade.

Table 3. Comparison of electrochemical properties of some metal oxides for alcohol oxidation.

| Electrode material | Current collector | Loading | Methanol concentration [M] | Scan rate [mV s⁻¹] | Anodic potential [V] | Peak current density [mA cm⁻²] | Ref. |
|--------------------|-------------------|---------|---------------------------|-------------------|-------------------|-----------------------------|------|
| NiO-MOF            | GCE               | 3       | 3                         | 50                | 0.8               | 275.85                       | [26] |
| Ni@3DHPGC⁴         | GCE               | –       | 0.5                       | 50                | 0.728             | 147.108                      | [33] |
| α-CoMoO₄ nanoflakes | Carbon cloth      | 0.5     | 0.5                       | 50                | 0.8               | 25                          | [54] |
| 2 wt%GO/Co-MOF     | GCE               | 3       | 50                         | 0.1               | 17.6              | 15.94                        | [55] |
| Ni/NiO/MWCNT       | GCE               | –       | 0.7                       | 50                | 0.43              | 15.94                        | [56] |
| NiO nanosheets     | GCE               | 0.285   | 0.5                       | 50                | 0.7               | 85.3                         | [57] |
| NCR                | Carbon cloth      | 0.2     | 1 m                       | 60                | 0.62              | 15                          | This work |
| NCR                | Carbon cloth      | 0.2     | 1 m ethanol               | 60                | 0.72              | 10                          | This work |

*Nickel encapsulated 3-dimensional hierarchical porous graphene.

Anodes. The synergic effect between two metal oxides and rGO increases the electrocatalytic performance. To increase the conductivity and enhance the electrocatalytic properties, the synthetic material was hybridized with rGO. The results showed that although both NC and NCR nanocomposites are efficient in all three processes, the addition of graphene nanosheets increases the stability of the electrode in MOR and EOR and increases the specific capacity when applied as a supercapacitor electrode. Moreover, the NCR exhibits lower overvoltage, lower potential, and higher current density than NC in both MOR and EOR processes. The investigated nanomaterials show great promise in the field of clean energies and can be suggested for future energy devices.

4. Experimental Section

Chemicals and Apparatus: Cobalt chloride (CoCl₂·6H₂O), nickel chloride (NiCl₂·6H₂O), urea, and potassium hydroxide (KOH) were prepared from Merck. A solution of 5% Nafion was prepared from Sigma Aldrich. Other needed chemicals were used in their analytical grade.

X-ray diffraction (XRD) patterns were obtained by X’Pert PRO MPD PANalytical and also the morphology of the synthetic nanomaterials was studied by scanning electron microscopy (SEM) images through Hitachi Model S-3700N. Energy dispersive X-ray (EDX) elemental analysis was performed with the same device. Transmission electron microscopy (TEM) images were obtained using a Philips EM 2085. Electrochemical tests were also performed with galvanostat/potentiotstat PGSTAT302N (Metrohm).

Synthesis of Materials: Reduced graphene oxide was prepared according to the previous work.⁴ NiO-Co₃O₄ (NC) was prepared by a hydrothermal method. Amounts of 0.474 g of cobalt chloride (CoCl₂·6H₂O), 0.948 g of nickel chloride (NiCl₂·6H₂O), and 1.08 g of urea were added to 35 ml of deionized water and the mixture was stirred for 30 min. Then, the resulted homogeneous solution was put in a 50 ml stainless steel reactor and heated at 140 °C for 12 h. Next, the reactor was cooled down at room temperature and the mixture was washed several times with water and ethanol and dried for 4 h at 50 °C. After that, the resulting powder was annealed at 400 °C with a heating rate of 5 °C min⁻¹. The synthesis of NiO-Co₃O₄/rGO (NCR) was performed with the same procedure. The different amounts of graphene oxide powder were added to the precursors. Here, five materials were obtained for NCR with 0.01, 0.02, 0.03, 0.04, and 0.05 g of GO. According to the electrochemical results, the NCR containing 0.03 g GO was selected as the optimum material for characterization and future electrochemical tests. In the hydrothermal process, rGO and NCR were simultaneously synthesized.

Electrode Fabrication: A three-electrode system was applied to investigate the potential of NCR and NC for use in supercapacitor electrodes and methanol/ethanol fuel cell anodes. A platinum wire as the auxiliary electrode, Ag/AgCl as the reference electrode, and modified carbon cloth (1 cm²) with electroactive materials as a working electrode were used. The electrodes were fabricated in this system. For modification of the working electrode, a slurry containing 20 mg of each of NCR and NC materials in certain amounts of Nafion and isopropl alcohol was prepared and then put on the carbon cloth surface with a mass loading of 2 mg cm⁻². Finally, the fabricated electrode was dried at 50 °C for 6 h.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
Co₃O₄, ethanol oxidation, methanol oxidation, NiO, rGO, supercapacitors

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