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MAGNETITE-GRAPHENE BASED NANOCOMPOSITES IN ELECTROCHEMISTRY: A BRIEF REVIEW ON THEIR APPLICATIONS

(Nanokomposit Magnetit-Grafin dalam Elektrokimia: Ulasan Ringkas dalam Aplikasinya)

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Abstract

Magnetite incorporates graphene or its derivatives, graphene oxide, or reduced graphene oxide, has received significant attention for its superior features, such as unique structure and large surface area with great number of active sites. The nanocomposite is priorly used in biosensors and biomedical for drug study. Many researchers currently opt for the nanocomposite in various electrochemistry applications as the first-rate material for said applicative fields due to its environmental-friendly nature and inexpensive production cost. This paper reviews the advantages of magnetic graphene-based material and its applications. The scope of this review is to highlight important justifications of electrochemical applications. A comprehensive discussion of the nanocomposite's physical and electrochemical properties, as well as its stability and reusability, are presented.

Keywords: magnetite, graphene, electrochemical, eco-friendly, electrode

Abstract

Magnetit digabungkan dengan grafin atau produk derivasinya, seperti grafin oksida atau grafin oksida terturun mendapat kajian meluas kerana ciri unik komposit tersebut, misalnya kawasan permukaan yang luas dengan bilangan tapak aktif yang amat banyak. Pada asalnya, nanokomposit tersebut digunakan dalam bidang biosensor dan biomedik untuk terutamanya dalam kajian dadah. Kini, ramai penyelidik memilih nanokomposit ini dan mengaplikasikannya sebagai bahan utama dalam pelbagai bidang elektrokimia atas dasar mesra alam dan kos penghasilan yang murah. Dalam kertas kajian ini, kelebihan nanokomposit dan penggunaan dalam bidang elektrokimia diulas. Skop ulasan memberi penghujahan yang penting tentang bidang elektrokimia. Di samping itu, ciri-ciri fizikal dan elektrokimia nanokomposit tersebut dibincangkan secara mendalam selain daripada kestabilan dan kebolehgunaan semula bahan tersebut.

Keywords: magnetit, grafin, elektrokimia, mesra alam, elektrod

Introduction

Technological advancements in electrochemistry have gained remarkable growth over past decades recently for their constant developed applications. Electrochemical technique is predominantly an efficient and alternative solution to conventional spectroscopic and chromatographic techniques. It offers rapid analysis, low cost, selective sensitivity, and user portability while being environmentally friendly. To further improve the electrochemical technology, electrocatalysis was introduced, which attracted significant attention from researchers globally as an establishment since the new hybrid approach was introduced. Moreover, the typical unmodified electrode such as bare carbon electrode or bare gold electrode has a chemically fouling nature, poor chemical stability, low mechanical strength, and tend to agglomerate on its own [1, 2].

Graphene is known as one of the most interesting materials in the research field for its exclusive characteristics and potential applications in various fields [3]. It is as discrete as one carbon atom in size but still carries a greater surface area, twice larger than ordinary activated carbon [4, 5]. It has a honeycomb lattice arrangement, a primitive building block for other carbon allotropes, such as 0D fullerenes, 1D carbon nanotubes, and 3D graphite. The composite has the capacity to adsorb an assortment of aromatic biomolecules via p–p stacking interaction and electrostatic interaction, making them optimal materials for forming biosensors and loading drugs [6]. Graphene is further refined into graphene oxide for enhanced properties, such as boosted surface area and reactive sites from the addition of oxides functional groups. Hydrophilicity and high dispersibility of graphene make it popular in removing water pollutants; however, it is difficult to be separated from aqueous solutions [7].

Graphene oxide (GO) is a resultant of graphene sheet embellished with oxygen (-OH) functional groups to great negative charge density and hydrophilic character. Typically, GO is a natural insulator, where it has lured sizeable interest for its prospective applications as an electrically insulating material in electronics and can be applied as an adsorbent. Nevertheless, it could be a conductive material through adequate exposure to reducing agents such as hydrazine hydrate or sodium borohydride, reducing and defecting its sites to make it active [8]. It is a prime component in the field of chemistry because of its high surface area with many functional groups around the plane. The high surface area subsequently supports the oxygen reduction reaction [9, 10]. The existence of functional groups on the GO plane produces a high negative charge density, larger surface area, and hydrophilic character.

Diminishing the oxygen-based functional groups in sheets of graphene oxide by in-situ reduction produces reduced graphene oxide (rGO). It is a better choice of using rGO as compared to GO in the aspect of electrochemistry. The reduced oxygen in GO sheets promptly increases Π-Π interaction by increasing sp^2 carbons [11, 12]. With these properties, a study was conducted to foresee the strong interaction between graphene and nanoparticles, especially with magnetic properties, which resulted in a salient potential with exclusive and enhanced functionalities useful in several applications [13].

Magnetic nanoparticle (MNP) utilised in electrochemical activities is known for its decent theoretical value, inexpensive production, and environmentally friendly. Together with magnetic properties, it has metallic properties that can conduct good electricity. Iron oxide nanoparticles, scientifically known as magnetite, are the utmost explored metal-based magnetic nanoparticles up to date. It turns to superparamagnetic once the ferrite particles become smaller than 128 nm. This averts self-agglomeration since they display their magnetic behaviour only when an external magnetic field is implemented [14]. However, inferior cycling stability, vulnerability to air oxidation, and agglomeration caused by imbalanced electron transfer occur easily. Therefore, merging of magnetite with carbon related materials, especially graphene (for its unique properties) into a nanocomposite was researched [15]. This technically increased the surface area and performed better electrochemical reactions when utilised in applications. With current findings, the nanocomposite can be further utilised for various applications, such as in big energy production plants. This changes the current perspective in the energy production field. More than 51% of global energy production is produced from non-renewable energy resources, to an option of renewable energy source that saves cost [16, 17].

The integration of magnetite-graphene plays a pivotal role in the electrochemical efficiency of a cell, other than to ensure the excellency of characteristics and longevity of nanocomposite while possessing better stability in terms of thermal and conditioning. This is based on the increase of electrical conductivity [18]. Generally, the development of magnetite-graphene nanocomposite begins with the synthesis of graphene oxide via modified Hummers' method [19] followed by the synthesis of MNP using a facile one-pot method or chemical induction method. This combination has been used in various fields such as biosensors, data storage, bioseparation, targeted drug delivery, coating from corrosion, and energy production [20]. The nanocomposite showed a great response in the biomedical field through excellent detection capability in sensor application, which proves to be an optimal substrate for surface immobilisation. This characteristic can be further explored and enhanced in targeted detection apart from the biomedical field, such as water pollution sensors.

Applications of Magnetic Graphene Nanocomposite

Batteries

Batteries, the handy energy storage material is a common material in daily life. It can be categorised into three types which are lithium-ion battery (LIB), sodium-ion battery (SIB), and lithium/sulphur-ion battery (LSIB) [21-23]. Among these, LIB is more preferably used for its exclusive features such as high energy density, high voltage, lightweight, and long life-cycle. The first LIB was introduced in 1991 by Sony Inc., and extensively used as handily and portable power source for electric and electronic devices [24]. This type of battery also has attracted attention in aerospace application as well as in military-based devices. As for the working principle of rechargeable batteries, it contains two electrodes, an anode (negative electrode) and a cathode (positive electrode). The cathode, as the lower capacity electrode, determines the overall capacity of a battery. Different types and structures of the separator component have been introduced. It primarily serves to physically separate the electrodes to prevent shorting while providing porosity for lithium-ion flow during charge and discharge [25]. In the discharging process of LIB, lithium-ion moves from the negative electrode to the positive electrode through an electrolyte and vice versa during the charging process. The process of ion movement is illustrated in Figure 1. Generally, the positive electrode in LIB is an intercalated lithium compound, while various materials have been developed for the negative electrode to increase the properties of the lithium-ion battery [26].

Magnetite developed into one of the promising active materials for anode of LIB due to the highest theoretical capacities (926 mAh/g) [27], which shows that Fe_3O_4 can react with eight lithium ions per formula unit compared to the currently used graphite anode with 372 mAh/g of capacity [28]. Apart from that, magnetite also possesses higher conductivity ($\sigma = 2 \times 104\ Sm^{-1}$) than most of other metal oxides [29] due to its magnetic properties [30]. However, a stand-alone magnetite nanoparticle is not significant for the Li-ion batteries' application due to its poor cyclic performance and rate capability, which causes aggregation of the composite and fluctuation of volume during the insertion or the extraction process of Li-ion. Furthermore, this anode exhibits intrinsic large electrochemical polarisation upon cycling, which reduces the system's 'round trip efficiency' and electrochemical reversibility. This is primarily due to poor electronic and ionic conductivities of Fe_3O_4 and slow solid-state diffusion of Li ions in this anode [31]. The low conductivity of composite also may lead to a rapid degradation process.

To add on, the combination of graphene with magnetite boosts the electrical properties and increases surface area, leading to exceptional thermal conductivity (~5000

W/mK). The extremely high values of thermal conductivity suggests that graphene can outperform carbon nanotubes (CNTs) in heat conduction. 2D nanosheets structure of graphene constitutes abundant active sites and accessible surfaces where it enables energy storage materials to achieve high power and energy density [32]. It is supported that the theoretical capacity of graphene (744 mAh/g) is twice as much as that of graphite because graphene can accommodate two Li-ions, instead of one for graphite, in each hexagonal loop of carbon (Li_2C_6). Thus, incorporating magnetite with graphene can overcome the aggregation of magnetite nanoparticles as the high surface area (2620 m^2/g) graphene will help the nanosized magnetite bind to its nanosheets. The large-volume variation of magnetite during the discharge-charge process also can be mitigated through the high surface area graphene [33]. The strategies of coating the magnetite nanoparticles to graphene enhance the electronic conductivity and boost the conversion yield as the metal integration of the magnetite possess an excellent magnetic property. Based on Huang et al. [34] combination of magnetite and graphene leading to the high Fe_3O_4 loading and outstanding cycling stability (83 per cent retention of the initial reversible capacity after 40 cycles) generated by the volume buffering effect of graphene sheets, the discharge capacity was increased to 750.0 mAh/g. This improved Fe_3O_4/graphene composite with improved performance could have a promising future in lithium-ion battery applications [35].

According to Kai Zhu et al. [36], it was observed that there was no capacity loss and better cycling stability of the improved batteries using nanocomposite. The discharge/charge rate of the battery increased while the Coulombic efficiency reached more than 95%. The nanocomposite supported short diffusion between electron transfer which indicated the enhanced conductivity of the battery. Previous works using various magnetite-graphene nanocomposites and their derivatives nanocomposites on lithium-ion batteries are tabulated in Table 1.

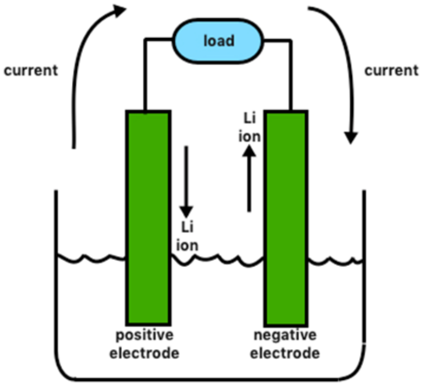

Figure 1. Discharging process of lithium-ion in lithium-ion battery

Table 1. Comparison of fabricated graphene-magnetite for lithium-ion battery application

Anode Materials	**Current Density (mAg^{-1})**	**Discharge Capacity ($mAhg^{-1}$)**	**Reversible Capacity ($mAhg^{-1}$)**	**Coulombic Efficiency (%)**	**Refs.**
Tight anchoring Fe_3O_4/Graphene	50	1133	1045	100	[30]
Gelatin-functionalized graphene decorated with iron oxide	100	1096	924	99	[36]
Fe_3O_4/Gr nanoparticles	-	920	-	96	[21]
Fe_3O_4/trigol reduced graphene	100	1880	1024	91	[37]
N-doped carbon coated Fe_3O_4	-	1173	800	99	[38]
3D hierarchical Fe_3O_4/Graphene	92.5	1114	609	92.5	[20]
Reduced graphene oxide@ nitrogen doped carbon	-	409.4	-	100	[26]
Fe_2O_3/rGO	1000	-	1242	97	[39]

Fuel cell

Fuel cell has been a source of energy generation for the past few decades. It has been recognised as the most efficient substitute for fossil fuels [44]. Sir William Robert Grove invented the first fuel cell by developing a wet-cell battery that depended on the electrochemical reaction that split water into hydrogen (H^+) and oxygen (O^-) ions. Since then, many other types of fuel cells have been invented and applied as a source of energy which contributes less pollution compared to other methods. Commonly used fuel cells include alkaline fuel cells, solid oxide fuel cells, microfluidic fuel cell, proton exchange membrane fuel cell, microbial fuel cell, and many more [45, 46]. The concept of fuel cell is the movement of electrons from cathode to anode. In general, hydrogen atoms enter a fuel cell at the anode, stripped of their electrons by a chemical reaction. The hydrogen atoms become "ionised," or electrically charged. Negatively charged electrons carry electricity across wires, allowing work to be done. The DC output of the fuel cell must be channelled via a conversion device called an inverter if alternating current (AC) is required. The cathode is where oxygen enters the fuel cell and then combines with electrons returning from the electrical circuit and hydrogen ions that have gone through the electrolyte from the anode in some cell types (like the one seen above). In other types of cells, oxygen picks up electrons and then travels through the electrolyte to reach the cell membrane. The best part of the fuel cell is that it is a renewable energy resource, easy to be constructed, and environmentally friendly, where no mass land destruction needs to be done to build platforms for other renewable resources such as windmills and hydro turbines. Fuel cell does not stop working as long as fuels (e.g., hydrogen, which is often used) and oxidants are supplied to the anodic chamber and cathodic chamber. The hydrogen oxidises at the anode where the reaction is called hydrogen evolution reaction (HER). At the same time, the oxygen is being reduced at the cathode, and the reaction is known as oxygen reduction reaction (ORR).

ORR at the cathode proceeds proceeds mainly through two pathways: indirect two-electron reduction (equation 1 and 2) and direct four-electron reduction (equation 3). The four-electron reaction is preferable because it does not produce peroxide species in the reaction as the reactivity of H_2O_2 is relatively higher than the stability of H_2O produced in the direct reaction [47]. The direct reaction also has higher operating potential and current efficiency as compared to the indirect reaction. But in general terms, hydrogen atoms enter a fuel cell at the anode, where a chemical reaction strips them off their electrons. The hydrogen atoms are "ionised" and carries a positive electrical charge. The negatively charged electrons provide the current through wires to do work. If alternating current (AC) is needed, the DC output of the fuel cell must be routed through a conversion device called an inverter. Oxygen enters the fuel cell at the cathode. In some cell types (like the one illustrated above), it combines with electrons returning from the electrical circuit and hydrogen ions that have travelled through the electrolyte from the anode. In other cell types, oxygen picks up electrons and then travels through the electrolyte to the anode, where it combines with hydrogen ions. The electrolyte plays a key role. It must permit only the appropriate ions to pass between the anode and cathode. If free electrons or other substances travel through the electrolyte, they will disrupt the chemical reaction whether they combine at anode or cathode, together with hydrogen and oxygen form water, which drains from the cell. As long as a fuel cell is supplied with hydrogen and oxygen, it will generate electricity.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad (2)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (3)$$

The overall performance of the fuel cell is mainly dependable on the electrode applied. Therefore, the exceptional material such as graphene is opted as the appropriate electrode for fuel cell. Noticeable high electrical conductivity features of graphene aids to smoothen the flow of ions and charge transportation in the fuel cell. Graphene's sp2 hexagonal lattice structure exhibits a high specific area which contributes to high capacitance value in the fuel cell and can be easily used as electrode for both application of HER and ORR [48, 12]. Graphene also possesses a high carrier mobility with a value of 2x10^{-5} $cm^2/V/s$, high mechanical strength, high transparency (~97.7%), and is also thermochemically stable.

The highly abundant iron oxide is acknowledged as a low-cost material to replace the conventional Pt electrode which make it one of the main reasons of usage in fuel cell application. Iron oxide possess excellent magnetic properties and high selectivity towards the oxygen reduction reaction [49, 50]. However, during the synthesis process of iron oxide, the composite tends to agglomerate due to uncontrollable growth of magnetite ion thus resulting in depleting performance in ORR and HER. In order to prevent such problem, use of carbonised materials as support to magnetite are very convenient. The incorporation of graphene with iron oxide will decrease the agglomeration of iron oxide. The efficient catalytic activity can also be achieved through the positive synergistic coupling effect between graphene and magnetite particles. Table 2 below shown the reaction pathway of composite in ORR.

Table 2. Reaction pathway of composite in ORR

Composites	**Reaction Pathway**	**ORR Potential (V)**	**Reaction Kinetics**	**Refs.**
α-Fe_2O_3/GO	3.2 to 3.4	-0.3 to -0.5	-	[51,52]
Fe_2O_3/ carbon	3.6	-	-	[53]
$FeO_{1.4}$/N-C	3.1-3.3	-0.056	-0.40 to -0.55	[54]
Fe_3O_4/N-Gas	4	-0.19	-0.19 to -1.2	[55]
Fe_3O_4/N-GSs	2	-0.26	-0.26 to -0.62	[55]
Fe_3O_4/N-CB	2	-0.24	-0.24 to -0.60	[55]
Fe_3O_4-CNx-Lys	3.4-3.6	-0.25	-0.25 to -0.45	[56]

Corrosion

Corrosion is a natural process that converts a refined metal into a more chemically stable form, and the process is well-known for the gradual destruction of materials by chemical and electrochemical reactions with the environment as the corrosive medium. Protection from corrosion is important to prevent structural and material damage. Corrosion also poses a threat towards public health and safety. Many types of organic-based coatings have been used to reduce corrosion of metal surfaces, as such epoxy coatings. However, these coatings only protect the top layer of the metal surface and are permeable to corrosive electrolytes' exposure. Hence, corrosion does occur underneath the epoxy coating [57]. To add on, the epoxy coating was attached to the applied surface through hydrogen bonding, where the stability reduces by time and is vulnerable to wet conditions. Shielding effect of the corrosion coatings is essential as its function is to block the contact between the substrate interface with the corrosive medium such as oxygens or sulfates and impede the diffusion of the corrosive medium to the protected metals through the anti-corrosion coatings [58]. This shielding effect can be increased by a uniform distribution of the anti-corrosive materials [59].

The high dispersibility and ultra-thin two-dimensional structure of graphene formed a barrier and increased the shielding effect. Apart from that, graphene has also become one of the promising corrosion protection due to its characteristics, which is impermeable to almost all molecules and ions [56]. It is believed that graphene is a revolutionary material in the field of corrosion protection because, as corrosion protection pigments, graphene is able to simultaneously improve the wear resistance, barrier properties, thermal conductivity, mechanical properties, and thermal stability of polymeric coatings [60]. The uniform dispersion and orientation of graphene parallel to the metal surface make it one of the promising materials for anti-corrosion coatings [61]. Graphene also retains a high adhesion force to enhance the bonding strength between the corrosion protecting coatings with the metals as a strong bonding force material able to hinder the accumulation of oxygen and sulphates at the metals interface and disrupt the corrosion process. A remarkable conductivity of graphene also helps to improve the cathodic protection effect of zinc-rich coatings on metal which an active zinc powder was used to formed corrosion couple with the protected metal interface.

The strength of corrosion protective layer against corrosive medium is determined by the angle of anti-corrosion materials with the substrate interface. A narrower angle of the materials with substrate will toughen the barrier of corrosion protective layer [62]. Thus, only graphene parallel to the surface obeys the shielding effect theory; meanwhile, the graphene perpendicular to the substrate interface did not provide the shielding effect. Therefore, a magnetic field-induced orientated alignment of magnetic graphene was introduced by loading magnetite onto the graphene surface. The magnetised graphene was movable under the action of the external magnetic field. It could also be horizontally aligned in the epoxy resin by the magnetic torque applied to the magnetic graphene sheet by the horizontal magnetic field, as shown in Figure 2 [63]. Moreover, the integration of magnetics with graphene is helpful as the magnetic effect increases the stability of the layer on the surface of metal applied [64].

Numerous works on magnetite graphene as a corrosion protective layer have been published in the past few years. One of the works demonstrated by Nayak *et al.,* deployed a graphene coated Ni film with effectiveness up to post annealing of 500 ^{0}C. Another study found that the use of graphene-coated Cu (111) surface, confirms that no corrosion is detected after the annealing process. Meanwhile, Anisur et al., stated a CVD graphene growth on nickel has improved corrosion resistance to 700 kΩcm^2 with the absence of hydrogen during the graphene growth process. Besides that, Fronczak et al., investigated the corrosion resistance of carbon-encapsulated iron nanoparticles with the use of nitric acid as corrosion agent. as it releases a large amount of Fe and exhibits a high corrosion resistance and high effectiveness up to post-annealing of 450-500 ^{0}C [65-67]. In addition, graphene-coated Cu and graphene-coated Cu/Ni alloy foil by CVD under heating for four at 200 °C in laboratory air, and immersing into a solution of 30% hydrogen peroxide, up to 45 minutes showed no changes to the surfaces. In contrast, bare Cu/Ni turned a dark shade of brown onto its surface [68]. It is shown that the presence of graphene in transition metal can act as anti-corrosive and protect the surface from damage. However, there is a challenge in this field, where the existence of defects may ruin all the advantages of graphene films acting as corrosion inhibitor. Table 3 illustrates the corrosion potential among the previous research on magnetite and graphene-based.

Table 3. Corrosion Potential (E_{corr}) Values obtained from potentiodynamic polarisation test

Composite	**Conditions**	**E_{corr} (mv)**	**I_{corr} (µA cm−1)**	**C_R (mm/year)**	**Refs.**
Bare carbon steel	In 3.5% NaCl	−530.89	95.0	1.103	[69]
Fe_3O_4	In 3.5% NaCl	−559.45	46.7	0.542	[69]
Fe_3O_4/PANI	In 3.5% NaCl	−598.69	3.0	0.035	[69]
Ni	In 3.5% NaCl	−481.0	6.138	2.605	[70]
Ni-GO1	In 3.5% NaCl	-424.0	4.845	2.055	[70]
Magnetite NPs (blank)	In 1M HCl, 30°C	−558.2	1.13	-	[71]
Magnetite NPs (0.1%)	In 1M HCl, 30°C	−588.6	0.021	-	[71]

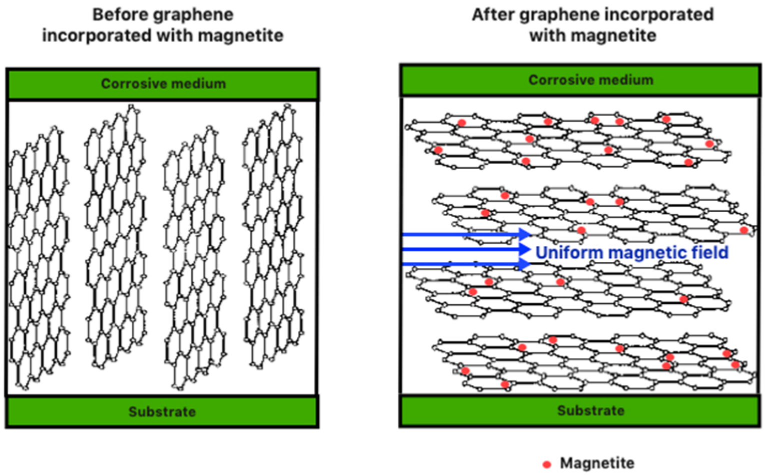

Figure 2. Perpendicular distribution of graphene without magnetite and parallel orientation of magnetite graphene in uniform magnetic field

Sensor

Electrochemical sensors work on the basis that an electrical current travels through a sensing electrode as a result of an electrochemical reaction that occurs at the surface of a sensing electrode coated with a catalyst, such as platinum. An electrochemical sensor consists of a metallic anode and a metallic cathode that are submerged in an electrolytic solution (such as H_2SO_4) to allow ion movement between the two electrodes. Electrochemical sensors typically have two or three-electrode designs with a membrane for gas transport. The electrical current is proportional to the hydrogen concentration, which may be monitored to determine the gas concentration [74]. An electrochemical sensor detects and analyses a specific compound by measuring the chemical signals produced from the electrochemical system and converting them into digital signals or well-known as chemical signals. These signals can be measured by analysing the current, potential, and conductance changes being emitted from the system [75]. The response obtained in the electrochemical sensor is due to the interaction between the electron transfer of the analyte in the electrolyte and the electricity being applied to the electrochemical system based on potentiometric, amperometric, voltammetric or conductivity measurements. The two most common electrochemical sensor configurations are amperometric and potentiometric sensors. Amperometric sensors work with a constant applied voltage, and the sensor signal is current. In contrast, potentiometric sensors work with zero current, and the sensor signal is the potential difference between the sensing electrode and a reference electrode [74]. The attraction of applying electrochemical sensors is based on their high sensitivity, good selectivity, cost-effectiveness compared to the conventional method, nature-friendly, simple pre-treatment process and fast analytical period [15].

In the application of electrochemical sensors, it is crucial to have excellent electron transfer properties to promote the ability of some enzymes and exceptional catalytic behaviour towards small biomolecules; and graphene with outstanding electron mobility (200,000 cm^{2}V^{-1}s^{-1} at electron density ~2x10^{11} cm^{-2}) can fulfil this critical requirement [76]. Graphene also possesses a less weighty graphene chemical sensor that is wearable and operates at normal atmospheric pressure and room temperature, making it cost-effective and low environmental impacts material [79].

Meanwhile, magnetite based-electrochemical sensors have shown to be an excellent choice for highly sensitive sensing with a linear range of several orders of magnitude [79]. Magnetite possesses distinguished properties which one could benefit from. However, it suffers from agglomeration due to its high surface energy and poor conductivity. Therefore, incorporating magnetite and graphene will enhance the conductivities of magnetite nanoparticles, reduce the agglomeration, improve the effective surface area and accelerate the rate of electron transfer across the electrode surface. This will eventually promote the sensitivity and stability of the analytical response [77, 78]. Table 4 outlines the graphene-magnetite modified electrode in electrochemical sensor application.

Table 4. Graphene-magnetite modified electrode in electrochemical sensor

Electrode	Analyte	Detection Method	Detection Limit	Linear Range	Refs.
C-rGO/Fe_3O_4	Dopamine	CA	7.00 nM	0.01 – 100.55 µM	[80]
Fe_3O_4/r-GO	Dopamine	DPV	0.08 µM	0.40 – 3.50 µM	[81]
Fe_3O_4/r-GO	H_2O_2	CV	6.00 nM	0.02-19.00 µM	[81]
CR-GO	H_2O_2	CV	0.05 µM	0.05 – 1500 µM	[82]
Fe_3O_4-Au/HRP	H_2O_2	CV	12.00 µM	0.02 – 2.50 mM	[83]
Fe_3O_4/GO	Prostate Specific Antigen (PSA)	Amperometric	15 fg/mL	0.1 – 1000 nM	[84]
Fe_3O_4/GO	Prostate Specific Membrane Antigen (PSMA)	Amperometric	4.8 fg/mL	1 – 10000 nM	[84]
Fe_3O_4/r-GO	NADH	CV	0.40 µM	15.00-190.00 µM	[81]
CR-GO	NADH	CV	10.00 µM	40.00-800.00 µM	[82]

Super-capacitor

As a type of electrochemical energy storage device, supercapacitors have received considerable attention because of their high-power density, fast charging/discharging rate, long cycle life, and low equivalent series resistance. A supercapacitor is ideal for numerous applications such as portable devices, electric vehicles, and flexible electronic devices [85]. Many parts make up a supercapacitor, including current collectors, electrodes, electrolytes, and separators. The separator's function is similar to that of the battery's separator. It isolates the two electrodes, allowing ions to travel through while preventing a short circuit between them. The basic principle of supercapacitor energy storage is to store electrical energy via an electric double-layer capacitance generated by charge separation at the electrolyte-bath solution interface [86]. Depending on the charge storage mechanisms, supercapacitors are divided into two main categories, including electrical double-layer capacitors (EDLC), which are based on the charge storage mechanism at the electrode/ electrolyte interface [87] and pseudocapacitance that relies on fast and reversible redox reaction that occurs at the surface of active materials [88, 89]. Electrostatic double-layer capacitors (EDLCs) use carbon electrodes or derivatives electrode-electrolyte (non-faradaic process) [90], while electrochemical pseudocapacitors use metal oxide or conducting polymer electrodes, reversible redox reaction (faradaic process) [91] with a high amount of electrochemical pseudocapacitance additional to the double-layer capacitance. By extending the electrode–electrolyte contact with nanomaterials with large specific area, the EDLC contribution can be boosted even more [92].

The distinctive properties of graphene will enhance the flexibility of the electrode and provide maximum adhesion with minimal distance between the electrode and electrolyte interface; thus, the charge-storage mechanism will eventually be more efficient [93]. However, to further improve the performance of supercapacitor, a nanosized transition metal oxide incorporated with carbonous material is one of the promising solutions.

The incorporation of magnetite with graphene reduces the aggregation of Fe_3O_4 nanoparticles as the native magnetite is found to be low conductive. Thus the capacity of magnetite-based supercapacitors is easily faded [96]. To overcome this problem, most of the Fe_3O_4 nanoparticles will be attached onto the surface of graphene therefore, the immobilisation of the magnetite particles on the surface of graphene would eventually lower the intensity of the aggregation as graphene had high conductivity and more electrochemical stability. Magnetite-graphene composite considerable as excellent electroactive materials as the composite being composed of 30 Fe_3O_4/r-GO bilayers which reported from Wang *et al.,*., 2014 being synthesised through a layer-by-layer self-assembly method on silicon or indium tin oxide (ITO) substrate and it provides the capacitance, C_s of 151 Fg^{-1} at 0.9 Ag^{-1} [97]. Another work reported by Wang *et al.,*., 2014 provide a capacitance, C_s of 220.1 Fg^{-1} at 0.5 Ag^{-1} by the production of magnetite-graphene via hydrothermal reaction method [98]. Table 5 displays different composites of magnetite graphene used as supercapacitors. Moreover, Table 6 below illustrates advantages, disadvantages and challenges in each application, batteries, fuel cell, corrosion, sensor and supercapacitors

Table 5. Different composites of magnetite graphene used as supercapacitor

Electrode Materials	**Current Collector**	**Electrolyte**	**Highest Specific Capacitance (Fg^{-1})**	**Current Density (Ag^{-1})**	**Refs.**
Multilayer rGO	Au-sputtered	PVA/H_3PO_4	247.3	0.176	[99]
Graphene hydrogel	Au-coated PI	PVA/H_2SO_4	186.0	1.000	[100]
CNT-graphene/Fe_3O_4 nPs	Au-coated PET	Filter paper/Na_2SO_4	200.4	1.000	[101]
Hollow Carbon Sphere/Fe_3O_4	Stainless steel	5M LiCl	193	1.000	[102]
Fe_3O_4/C core shell microsphere	-	1M KOH	110.8	0.500	[103]

Table 6**.** Summary of advantages, disadvantages and challenges between applications

Applications	**Advantages**	**Disadvantages**	**Challenges**	**Ref.**
Batteries	High electrical conductivity, big Li^+ storage capacity, greater reversible capacity, high-rate performance, and cyclic stability.	Large surface area of rGO tends to restack, causing passivated solid electrolyte interface (SEI) film forms and irreversible electrolyte consumptions, resulting in capacity fading and low Coulombic efficiencies	Fabricating three-dimensional (3D) rGO or porous rGO to reduce agglomerations of graphene sheets and increase the active surface area, resulting in fast diffusion	[40-43]
Fuel cell	Surface of the electrocatalyst will not be inactivated prematurely. The catalyst is easy to recycle, which saves money and protects the environment	Graphene sheets tend to restack due to the attractive forces between graphene sheets, leading to a decrease in the availability of active sites	The choice of carrier material is key to the activity, selectivity, durability and cost-effectiveness of a catalyst.	[43]
Corrosion	Preventing the transport of corrosive or oxidative species toward the underlying substrate without notably altering its thermal conductivity and optical properties	Poor adhesion of graphene-based coatings to the most engineering metals	Graphene-based coatings produced directly on metallic surfaces do not improve corrosion protection	[72, 73]
Sensors	High sensitive sensing with a linear range magnitude nanoparticles can be highly dispersed on its surface, and the charge transfer at the interface of these hybrid materials can provide a synergistic effect	Decreasing interfering species' non-specific adsorption, and (3) maintaining the sensor's repeatability and stability in complicated actual matrices	Sensitive to temperature and, therefore, the sensors typically are internally temperature compensated greater the exposure to the target gas, the shorter the life span	[79, 80]

Table 6 (cont'd). Summary of advantages, disadvantages and challenges between applications

Applications	Advantages	Disadvantages	Challenges	Ref.
Super Capacitors	Can be coupled to generate hybrid nanostructures with EDLC and pseudocapacitive capabilities. Adding Fe_3O_4 to the anode boosted both the power output and the anodic capacitance	Poor electrochemical stability and had low conductivity	Limitations in transferring capacitive (F) performance values to bigger scales or commercial devices that retain the desirable properties of EDL SCs that outperform the current supercapacitor generation	[40-43]

Stability and Reusability

The stability and reusability of the magnetite graphene nanocomposite are important aspects to be considered to avoid any loss of cost and energy. The magnetite graphene composite seems to be potential material to supplement the techniques in use due to particular characteristics such as selectivity, low building and storage cost, miniaturising potential, easy automaticity, and simple to build and portable apparatus.

For example, work using batteries application as described by Li et al. revealed that the capacity of the magnetite graphene composite was ~434 mAhg^{-1} after 50 cycles which is still 61% of the initial capacity (709.6 mAhg^{-1}) [105]. Another work presented by Zhou et al., uses graphene wrapped Fe_3O_4 nanoparticles for anode materials in applying lithium-ion batteries. The charge capacity of the magnetite graphene remained at 950 mAhg^{-1} from the initial capacity even after the 85th cycle which demonstrates the improvement of cycling stability of the composite. The Coulombic efficiency of the magnetite graphene after the second cycle remained close to 100% until the 30th cycle. The magnetite graphene composite is also reported to exhibit an outstanding cyclic ability where it retains 91% of its initial capacity after 100 cycles when tested at a higher current density of 700 mAhg^{-1} [106].

Based on the work conducted by Guo et al., which used magnetite modified graphene for oxygen reduction reaction (ORR) of fuel cell application, the composites exhibited outstanding stability and a four-electron transfer pathway, suggesting the direct reduction of oxygen to water. The nanocomposite decorated graphene also displayed superior oxygen reduction reaction activity with a half-wave potential of 0.85 V and 0.97 V of the onset potential, where the value is higher than the commercial 20 wt% Pt/C electrode [107].

On top of that, Vinodha et al. also used magnetite graphene as an electrode modifier for detection of hydrazine, The stability of Fe_3O_4-rGO were determined through the stability curves of the composite/GCE between the potential of negative 1 (-1) to positive 1 (+1) at a scan rate of 0.05 Vs^{-1} in 0.1M PBS solution. The composites reached their stable form at 30th cycle after continuous cycle. The redox peak current density decreased evenly before the 30th cycle. Once the magnetite graphene composite reaches its stable form, the stability of the composite remains until the 35th cycle. The reproducibility and reusability properties remained 95.16% from the original detection limit after a gap of 20 days of analysis [108, 109-111].

Long term stability of magnetite graphene composite also has been reported by Ghasemi et al., which used the composite for supercapacitors application. The composite being tested for 500 cycles by repeating the charge/discharge test, and during the first 100 cycles, it is being observed that it is only a slight increase, and the composite remains 87% of the initial capacitance after 500 cycles and only 3% decay in the capacitance [89,111-113].

Future Perspectives

Magnetite nanoparticles decorated on graphene sheets require comprehensive understanding both theoretically and experimentally. To improve this aspect, researchers are encouraged to use advanced physical characterisation techniques to deeply comprehend the control of the iron oxide nanoparticles' shape, size, crystallinity, distribution, and phase composition onto the graphene sheets. It is recommended to study the electrocatalytic efficiency of the nanocomposite towards ORR that can be further analysed using RDE and RRDE voltammetry techniques, where exposure to hydrodynamic effect and kinetic parameter will be obtained. The synthesis and production of high-quality graphene sheets also need extra attention. The in-situ production may lead to several defects and low purity of product as the core is graphene before magnetite is embedded into the sheets. Small-scale consumption of the nanocomposite in the electrochemical field can be enhanced into big-scale production, which can be used in energy generation plants as a primary source of renewable energy. The appropriate storage of Fe_3O_4/rGO is vital to avoid any contamination towards the sample or oxidation process to maghemite or hematite. The nanocomposite can be used extensively in other fields other than energy production, such as biomedical imaging, wastewater treatment, or water pollution removal. The properties of the nanocomposite might boost and give better-targeted yield throughout applications. Magnetic graphene can be further studied for its usage in human body for bone regeneration surgery treatment. The nanocomposite can be further modified with the addition of different, non-metallic nanoparticles to prolong the lifetime of the nanocomposite and give an increase in surface area and added exceptional properties.

Conclusion

Most of the process to synthesise magnetic graphene oxide is environmentally friendly, obeying the green chemistry rule. Graphene oxide is used as a unique and excellent material in the research field. Magnetic compound integration into GO strengthens the nanocomposite with more active sites and a larger surface area. A various alternative has been found recently to overcome the dependency of fossil fuels that will deplete sooner in the current rate of usage. Fuel cell is the brainchild of scientists who have a more excellent prospect in future; however, not favoured due to high costs due to the requirement of expensive materials such as platinum for generation of energy. Small scale energy production such as batteries improved its efficiency by the usage of magnetite graphene oxide nanocomposite. In corrosion, the nanocomposite layer proved to be better in protecting metal surfaces. Use of magnetite graphene oxide nanocomposite also improvises any gadgets and instruments applied. The simple method of production that obeys the green chemistry rules makes the production of the nanocomposite is safer and can be done at low cost. This is important as it is beneficial to industries and developing countries to cut-cost of energy production mainly. The material would be the most applied compound in wider fields in the future.

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