

Graphene (Oxide) – Metal/Metal (Hydr)oxide Composites: Synthesis and Applications in Electrochemical Energy Storage and Conversion

by

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ABSTRACT

The massive energy demand in the world will be supplied by renewable energy sources (solar, wind, etc.) with the inevitable depletion of fossil fuels. However, efficient utilization of these sources heavily depends on the development of advanced energy storage and conversion devices due to their intermittent nature. In this regard, electrochemical capacitors, batteries, and fuel cells are the main electrochemical systems that can assist the continuous operation of the renewable sources, or offset the daily energy need individually. The common component in all the electrochemical energy devices is the electrodes which contain active material and the current collector. Physicochemical properties of the active material determine the overall device performance.

This dissertation is devoted to the synthesis of graphene oxide (GO) - metal/metal (hydr)oxide composite electrodes for electrochemical applications. In the first part, production of two-dimensional composite electrodes is presented as electrochemical capacitor electrodes. First row transition metal cations (Co^{2+} , Ni^{2+} , Mn^{2+} , Fe^{2+}) and GO were combined by utilization of simple electrostatic interactions. The highest capacitance was obtained with Fe/GO (38.7 mF cm^{-2}) followed by rCo/GO (31.6 mF cm^{-2}) and rFe/GO (29.1 mF cm^{-2}) at 20 mV s^{-1} , where r represents electrochemically-reduced composites. The nature of the metal was influential in the charge-storage mechanism of the composites: while rCo/GO and rNi/GO were governed by diffusion-limited processes, rMn/GO and rFe/GO showed pseudocapacitive behavior. Furthermore, ultrathin electrodes of Ni(OH)_2 and GO were produced via layer-by-layer assembly (LBL) followed by hydrazine vapor reduction to enhance electrical conductivity of GO. Reduced 9-bilayer $[\text{Ni(OH)}_2/\text{GO}]$ film exhibited areal capacitance of 8.6 mF cm^{-2} at 2 mV s^{-1} , 3-fold higher than that of LBL-assembled $[\text{CoAl LDH/rGO}]$ thin film reported in the literature. LBL-assembly was also utilized to produce superparamagnetic iron oxide nanoparticles (SPION)/GO thin films. State-of-the-art electron paramagnetic resonance results revealed the competition between carbon defect centers and Fe-related paramagnetic centers on the electrochemical performance. In fact,

reduced 1-bilayer [SPION/GO] had enhanced specific capacitance of 1570 F g^{-1} at 5 mV s^{-1} , outperforming all the LBL-assembled iron oxide/rGO films and most of the transition metal oxide/rGO composites in the literature. In all the LBL-grown composites, as-deposited films exhibited pseudocapacitive properties, whereas hydrazine-reduced films showed more diffusion-limited charge storage, like in batteries.

In the second part of the thesis, synthesis of graphene aerogels (GAs) is presented as the next-generation three-dimensional form of graphene. One-step hydrothermal treatment of GO solutions resulted in formation of high surface area GAs ($\sim 700 \text{ m}^2 \text{ g}^{-1}$) with the aid of supercritical CO_2 (scCO_2) drying. Obtained metal-free GA electrodes on nickel foam exhibited superior specific capacitance (390 F g^{-1} at 5 mV s^{-1}) than the counterparts reported in the literature. GAs were later decorated with metal nanoparticles as possible electrocatalysts for oxygen evolution (OER) and oxygen reduction reactions (ORR). Ni/GA composites were synthesized via one-pot hydrothermal reaction coupled with thermal reduction under H_2/He environment as possible OER electrocatalysts. By using urea as the continuous hydroxyl ion supplier during the hydrothermal reaction, Ni loading was tuned between 1.5 and 40 wt % in a highly-controlled fashion. Ni/GA with 40 wt % Ni exhibited low overpotential of 320 mV for the supply of 10 mA cm^{-2} which is 110 mV lower than that of 80 wt % Ni/GA and 50 mV lower than that of 20 wt % Ir/C and 20 wt % Ru/C reported in the literature. Lastly, Pt loaded GAs were synthesized by scCO_2 assisted deposition as possible ORR electrocatalysts. Pt nanoparticle size was varied from 1.2 to 2.9 nm by increasing the thermal conversion temperature from 400 to 800 °C. Simultaneously, gradual thermal deoxygenation of GA was observed. Obtained Pt/GA converted at 600 °C had enhanced electrochemical surface area of $102 \text{ m}^2 \text{ g}^{-1}$, which is higher than that of commercial Pt/C. Overall, the mass activities of Pt/GA electrocatalysts followed the order: $\text{Pt/GA(600)} > \text{Pt/GA(400)} > \text{Pt/GA(800)}$.

ÖZET

Fosil yakıtlarının engellenemez tükenişiyle beraber, dünyadaki muazzam enerji talebi sürdürülebilir enerji kaynaklarıyla (güneş, rüzgar, vb.) sağlanacaktır. Ancak bu kaynaklar sürekli çalışmadıkları için, verimli kullanımları ileri düzeyde enerji depolama ve dönüştürme aygıtlarının geliştirilmesine bağlıdır. Bu bağlamda, elektrokimyasal kapasitörler, piller ve yakıt pilleri, sürdürülebilir kaynakların kesintisiz çalışmasına yardımcı olabilecek veya tek başlarına günlük enerji ihtiyaçlarını karşılayabilecek ana elektrokimyasal enerji sistemleri olarak sayılabilir. Bahsedilen elektrokimyasal enerji aygıtlarının ana bileşeni olan elektrotlar, aktif malzeme ve akım kolektöründen oluşur. Buradaki aktif malzemenin fizikokimyasal özellikleri, oluşturulan aygıtın genel performansını belirleyen önemli bir parametredir.

Bu tez çalışması, elektrokimyasal uygulamalar için grafen oksit (GO) ve metal/metal hidr(oksit) kompozit elektrotların sentezlenmesine adanmıştır. İlk bölümde, elektrokimyasal kapasitörler için iki-boyutlu kompozit elektrotların üretimi sunulmuştur. Basit elektrostatik etkileşimler yardımıyla birinci sıradaki geçiş metal katyonları (Co^{2+} , Ni^{2+} , Mn^{2+} , Fe^{2+}), GO ile bir araya getirilmiştir. En yüksek kapasitans değeri sırasıyla Fe/GO (38.7 mF cm^{-2}), rCo/GO (31.6 mF cm^{-2}) ve rFe/GO (29.1 mF cm^{-2}) elektrotlarıyla elde edilmiştir (elektrokimyasal olarak indirgenmiş kompozitlerin başına “r” getirilmiştir). Kullanılan metalin cinsi, kompozitin yük depolama özelliklerini doğrudan etkilemiştir: rCo/GO ve rNi/GO elektrotlarının difüzyonla sınırlı kalırken, rMn/GO ve rFe/GO psödo-kapasitif özellik göstermiştir. Buna ek olarak, çok ince $\text{Ni(OH)}_2/\text{GO}$ elektrotları katman-katman bir araya getirilmiş ve GO’nun elektriksel iletkenliğini artırmak için, hidrazin buharında indirgenmiştir. İndirgenmiş 9-çift katmanlı $[\text{Ni(OH)}_2/\text{GO}]$, 2 mV s^{-1} tarama hızında 8.6 mF cm^{-2} kapasitans sergilemiştir; bu değer literatürdeki katman-katman bir araya getirilmiş $[\text{CoAl LDH/rGO}]$ ince filminden üç kat daha yüksektir. Katman katman bir araya getirme yöntemi, süperparamanyetik demir oksit nanoparçacıkları (SPION)/GO ince filmlerinin oluşturulmasında da kullanmıştır. En gelişkin elektron paramanyetik rezonans spektroskopisi,

karbondaki kusur merkezleri ve demirdeki paramanyetik merkezlerin elektrokimyasal performansı belirlemek için bir yarış içinde olduklarını göstermiştir. Sonuç olarak indirgenmiş 9-çift katmanlı [SPION/GO] filmi, 5 mV s^{-1} tarama hızında 1570 F g^{-1} spesifik kapasitansa ulaşarak literatürdeki bütün katman-katman bir araya getirilmiş demir oksit/indirgenmiş grafen oksit filmlerin ve geçiş metal oksit/GO kompozitlerin çoğunun önüne geçmiştir. Bütün katman-katman bir araya getirilmiş kompozitlerin analizinde görülmüştür ki, oluşturuldukları halleriyle psödo-kapasitif özellik gösteren elektrotlar, hidrazin ile indirgendikten sonra pillerde görüldüğü gibi difüzyonla-sınırlandırılmış yük depolama sergilemişlerdir.

Bu tez çalışmasının ikinci kısmında, grafenin gelecek nesil üç boyutlu formu olan grafen aerojellerin (GA) sentezi sunulmuştur. GO solüsyonlarının tek-aşamalı hidrotermal muamelesiyle ve süperkritik CO_2 (scCO_2) kurutmanın yardımıyla, yaklaşık $700 \text{ m}^2 \text{ g}^{-1}$ yüzey alanına sahip GA yapıları oluşturulmuştur. Nikel-köpük üzerine kaplanan GA elektrotları, literatürdeki benzer malzemelerden daha yüksek spesifik kapasitansa ulaşmıştır (5 mV s^{-1} tarama hızında 390 F g^{-1}). Sentezlenen GA'lar daha sonra metal nanoparçacıklarıyla donatılarak, oksijen oluşturma (OER) ve oksijen indirgeme (ORR) reaksiyonlarına olası elektrokatalizörler olarak kullanılmıştır. OER elektrokatalizörleri olarak Ni/GA kompozitleri, tek-aşamalı hidrotermal reaksiyon ve devamında H_2/He ortamında termal indirgenme yöntemiyle sentezlenmiştir. Ürenin kesintisiz hidroksil iyon sağlayıcısı olarak kullanımıyla, Ni yükleme miktarı kütlece yüzde 1.5 ile 40 arasında kontrollü olarak değiştirilmiştir. Yüzde 40 Ni içeren Ni/GA kompoziti, 10 mA cm^{-2} akım yoğunluğu için literatürdeki yüzde 80'lik Ni/GA'dan 110, yüzde 20'lik Ir/C ve yüzde 20'lik Ru/C'dan 50 mV daha düşük bir aşırıgerilim (320 mV) gerektirmiştir. Son olarak, olası ORR elektrokatalizörleri olarak Pt yüklenmiş GA'lar scCO_2 yardımıyla sentezlenmiştir. Pt nanoparçacık boyutu, termal dönüştürme sıcaklığını 400'den 800 °C'ye çıkararak 1.2 ve 2.9 nm arasında değiştirilmiştir. Eşzamanlı olarak, GA yapısı sıcaklık arttıkça termal olarak oksijenlerinden arındırılmıştır. Sentezlenen Pt/GA(600) kompozitinin, $102 \text{ m}^2 \text{ g}^{-1}$ gibi yüksek bir elektrokimyasal yüzey alanına sahip olduğu görülmüştür. Bu değer, ticari olarak kullanılan Pt/C'unkinden daha yüksektir. Diğer bir taraftan, Pt/GA

elektrokatalizörlerinin birim kütledeki aktiviteleri şu şekilde sıralanmıştır:

$\text{Pt/GA(600)} > \text{Pt/GA(400)} > \text{Pt/GA(800)}$.



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LIST OF ACRONYMS

AFM: Atomic force microscopy
APTMS: 3-(Aminopropyl)trimethoxysilane
ATR-IR: Attenuated Total Reflectance-Infrared
bPEI: Branched polyethyleneimine
CV: Cyclic voltammetry
EDLC: Electrical double layer capacitor
EDX: Energy-dispersive X-ray
EPR: Electron paramagnetic resonance
ESA: Electrochemical surface area
FESEM: Field-Emission scanning electron microscopy
GA: Graphene aerogel
GO: Graphene oxide
HER: Hydrogen evolution reaction
HOR: Hydrogen oxidation reaction
HRTEM: High-resolution transmission electron microscopy
ITO: Indium tin oxide
MWCNT: Multi-walled carbon nanotube
OER: Oxygen evolution reaction
ORR: Oxygen reduction reaction
RDE: Rotating disk electrode
rGO: Reduced graphene oxide
SC: Specific capacitance
sCO₂: Supercritical carbon dioxide
SPION: Superparamagnetic iron oxide nanoparticles
STEM: Scanning transmission electron microscopy
TOF: Turnover frequency
XPS: X-ray photoelectron spectroscopy
XRD: X-ray diffraction

Chapter 1: Introduction

1.1. Graphene and Its Derivatives

1.1.1. Graphene

Our life is dominated by carbon in all aspects. The two well-known allotropes of carbon are diamond and graphite. Single layer graphite, graphene, is the wonder material of the last decade with its extraordinary properties. [1] Graphene is composed of hexagonally arranged sp^2 -hybridized carbon network, in which carbons are bonded via σ -bonds in the lateral axis and the half-filled π orbital provides delocalization of electrons. Although σ -bonds provide mechanical integrity in the lateral axis, since there is no chemical bonding in the c-axis, out-of-plane interactions are extremely weak. [2] Graphene has excellent thermal conductivity ($4840\text{--}5300\text{ W m}^{-1}\text{ K}^{-1}$), extraordinary electron mobility ($> 2 \times 10^5\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$), high theoretical specific surface area ($2630\text{ m}^2\text{ g}^{-1}$), and high mechanical strength (tensile strength $\sim 130\text{ GPa}$, modulus $\sim 1000\text{ GPa}$). [1,3] Due to the afore-mentioned properties, hundreds of research groups study graphene's chemical and physical characteristics in both academia and industry. In this regard, Figure 1-1 exhibits evolution of the list of publications in the last 20 years including “graphene” in the title. From the physical discovery of single layer graphene in 2004 by Novoselov and Geim [4], the number of studies increased gradually. The researchers originate mainly from chemistry, material science, physics, and engineering who study graphene, albeit studies are generally interdisciplinary (Figure 1-1). Graphene can be obtained by several methods; these include mechanical exfoliation, unrolling carbon nanotubes (CNT), ultrasonic cleavage, epitaxial growth on SiC, chemical vapor deposition (CVD), thermal reduction, and chemical reduction. [5,6] Mechanical exfoliation is the cleavage of individual graphene sheets by mechanical pulling, also named as the “Scotch-tape” method. Although this technique produces defect-free graphene layers, scalability is almost impossible. Unrolling CNT includes treatment of CNT layers simultaneously with Li and NH_3

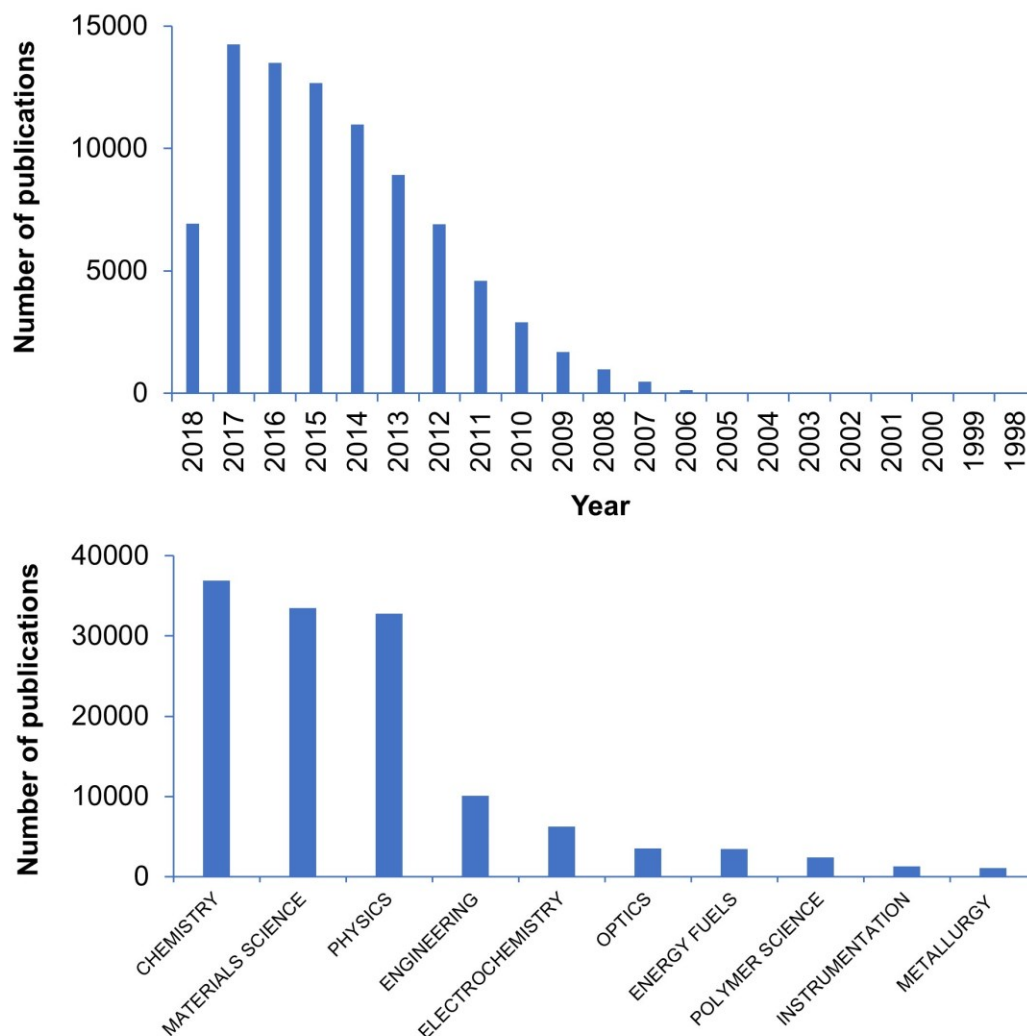


Figure 1-1 Number of publications that include "graphene" in the title categorized by (above) year and (below) discipline. Data taken from www.webofknowledge.com.

which results in exfoliation and unwrapping CNT to form graphene. Ultrasonic cleavage is the exfoliation of graphite powder in various solvents via sonication. The solvents generally include organic ones due to hydrophobic nature of graphene. Epitaxial growth on SiC proceeds with thermal desorption of Si on Si-terminated single-crystal H-SiC, resulting in the formation of 2-3 layer graphene. Again, production of large graphene domains is not feasible with this technique. CVD production of graphene generally includes flowing CH_4 at high temperatures (1000°C) on copper substrates. With CVD, large graphene domains can be synthesized on Cu. Thermal reduction requires heating of graphite with acids under pressure. Thermally expanded graphite

Table 1-1 Comparison of the characteristics of the synthesis methods of graphene

Synthesis method	Quality	Purity	Cost	Scalability	Yield
Mechanical exfoliation	High	Middle	Low	Very low	Low
Epitaxial growth on SiC	High	Middle	Middle	Low	Low
Chemical vapor deposition	High	Middle	Middle	Middle	Low
Ultrasonic cleavage	High	Middle	Low	High	Low
Chemical reduction	Low	Low	Low	High	Low

layers can be exfoliated if the pressure applied overcomes van der Waals forces connecting graphene layers. Lastly, chemical reduction is the oxidation of graphite with harsh oxidizing agents to produce graphite oxide followed by ultrasonic exfoliation of hydrophilic graphite oxide layers to form graphene oxide (GO). GO is later reduced with various methods (chemical, thermal, electrochemical) to produce graphene.

1.1.2. Graphene Oxide

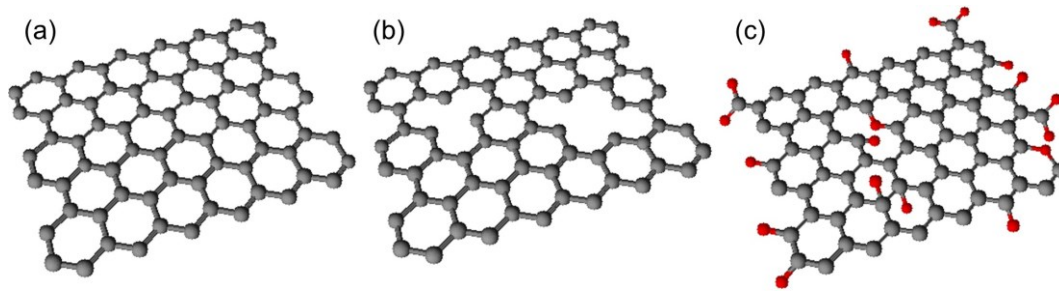
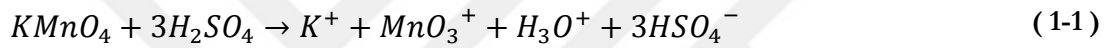


Figure 1-2 Chemical structure of (a) perfect graphene (b) graphene with defects and (c) graphene oxide

As mentioned in Section 1.1.1. , one of the most popular method to produce graphene is chemical reduction due to high scalability. In this technique, precursor graphite is first oxidized to produce graphite oxide powder. Chemical oxidation of graphite is first reported by British chemist B. C. Brodie in 1859. [7] Brodie used “potash of chlorate” (KClO_3) to oxidize graphite in fuming nitric acid (HNO_3). He later tried to determine the molecular weight of graphite stating:

“This form of carbon should be characterized by a name marking it as a distinct element. I propose to term it Graphon.” After 40 years of Brodie’s discovery, Staudenmaier improved the synthesis by addition of KClO₃ in smaller portions and changing the reaction medium to HNO₃+H₂SO₄ mixture. [8] At 1958, after 60 years of Staudenmaier’s report, Hummers and Offeman altered the oxidizing agent to potassium permanganate (KMnO₄) in concentrated sulfuric acid (H₂SO₄). [9] Up to date, hundreds of studies still utilize the synthesis method developed in 1958 by Hummers and Offeman, albeit with slight modifications. These new techniques are named as “modified Hummers method” every time a change is made. Although Hummers method proposed KMnO₄ as the main oxidizing agent, the actual oxidizer is dimanganese heptoxide formed in presence of strong acid by the following reaction [10]:



This red oil (dimanganese heptoxide) produces dark green liquid in contact with H₂SO₄. It ignites upon contact with any organic material (including ethanol) and explodes when heated above 55 °C. Thus, the synthesis of graphite oxide is carried out in an ice-bath until the completion of the addition of all KMnO₄. At the end, various functional groups are produced on the individual graphite layers including hydroxyls, epoxides, carbonyls, and carboxylic acids. The exact structure of the produced graphite oxide has been debated over decades, albeit the most widely accepted model is proposed by He et al. [11], also known as the Lerf-Klinowski model (Figure 1-3a). According to this model, carboxylic acids are present at the edges of the sheets, while hydroxyls and epoxides decorate the basal plane.

Graphite oxide can be exfoliated easily in water due to its high hydrophilicity via simple sonication resulting in production of single-layer graphite oxide, named thereafter graphene oxide (GO). The strong hydrogen-bonding formed between epoxides and hydroxides of GO layers (Figure 1-3b)

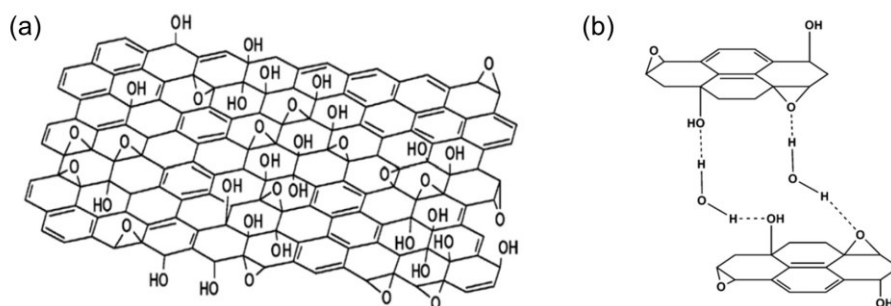


Figure 1-3 (a) Lerf-Klinowski model for the chemical structure of graphene oxide (b) Hydrogen bonding formed between graphene oxide and water [12,13]

and the electrostatic repulsion between the negatively charged GO layers are the main driving forces for the enhanced colloidal stability of GO solutions in water. [12]

1.1.3. Reduced Graphene Oxide

Production of reduced graphene oxide (rGO) from GO solutions can be conducted by several methods. Commonly used methods include: thermal reduction, photoreduction, electrochemical reduction, solvothermal reduction, and chemical reduction. [13] Thermal deoxygenation of GO is carried out under vacuum, inert atmosphere, or a reducing gas (H_2). [14] The reaction mainly proceeds with decomposition of functional groups to produce CO/CO_2 . The reduction degree (C/O ratio) and consequently, the electrical conductivity of the produced rGO depends on the reduction temperature and duration. [15] Overall, thermal deoxygenation of rGO is an effective but energy-consuming process. Photoreduction of GO sheets include irradiation of GO solutions with UV source under ambient or inert atmosphere. [16,17] The technique produces CO_2 and H_2 as a result of the photoreaction between GO and water induced by semiconducting character of GO nanosheets. Electrochemical reduction is a clean alternative to produce rGO via voltammetric or chronoamperometric techniques. At potentials more negative than -0.75 V (vs SCE), reduction of GO is observed. [18] Solvothermal reduction includes heating of GO dispersion in water or any other solvent above the boiling point in a closed vessel. The heat and pressure induce deoxygenation of GO layers in which the pH of the starting solution is effectual in the final dispersibility of rGO. [19] Last but not least, chemical reduction overcomes all other techniques

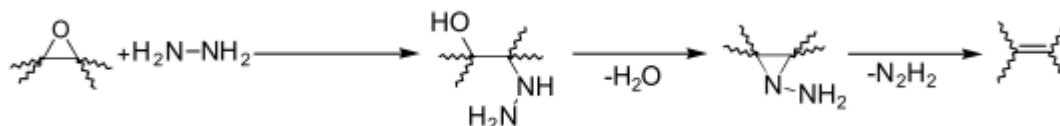


Figure 1-4 Proposed reaction mechanism for epoxide ring-opening via hydrazine attack [20]

in terms of effectiveness, energy consumption, and chemical diversity of the final product. Among the reducing agents commonly utilized (borohydrides, aluminum hydride, hydrohalic acid, L-ascorbic acid, pyrrole, etc.), hydrazine is the most widely preferred chemical. Hydrazine produces rGOs with high C/O ratio and electrical conductivity under relatively mild conditions ($\sim 85^\circ\text{C}$). Chemical reduction with hydrazine is proposed to be driven by the ring-opening reactions of epoxides (Figure 1-4). [20] Additionally, nitrogen doping occurs with the formation of pyrazoline or pyrazole groups during hydrazine reductions. [21]

1.2. Graphene and Its Composites for Electrochemical Applications

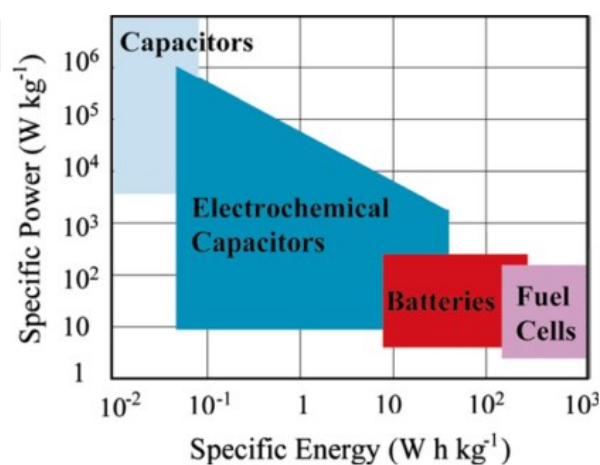


Figure 1-5 Ragone plot for various electrochemical energy storage devices [25]

Although graphene is widely utilized in various applications (field effect transistors, sensors, transparent conductive films, desalination membranes, solar cells, etc.), use of this wonder nanosheet for electrochemical applications is promising due to its enormous available surface area. [22,23] Utilization of graphene in electrochemical applications is also reflected in the number of

publications in the field of “electrochemistry”; around 6000 reports exist including “graphene” in their title (Figure 1-1b).

Table 1-2 Comparison of the typical characteristics of electrochemical capacitors, batteries, and fuel cells. Data taken from reference [24].

Characteristics	ECs	Batteries	Fuel Cells
Charge-discharge time	ms-s	1-12 h	1-300 h
Operating temperature / °C	-40 to +85	-20 to +65	+25 to +1000
Operating cell potential / V	2.3 - 2.75	1.25 - 4.2	0.6 – 1.0
Power density / kW kg ⁻¹	10 - 100	0.005 – 0.4	0.001 – 0.1
Energy density / W h kg ⁻¹	1 - 5	5 - 600	300 - 3000

Electrical energy storage devices dominate our world as alternative power sources, with the inevitable depletion of fossil fuels. These systems include fuel cells, batteries, and electrochemical capacitors (ECs), and conventional dielectric capacitors. [25] Ragone plot in Figure 1-5 compares the energy and power densities and Table 1-2 compares typical characteristics of these energy devices. Energy-density is the total energy that can be delivered by the system per unit mass/volume, while power-density is the energy provided per unit time (and mass/volume). Thus, power-density determines the “speed” and energy-density is related with the “amount” of the energy. In the Ragone plot, dielectric capacitors cover the high power-density region, whereas fuel cells dominate the high energy-density region.

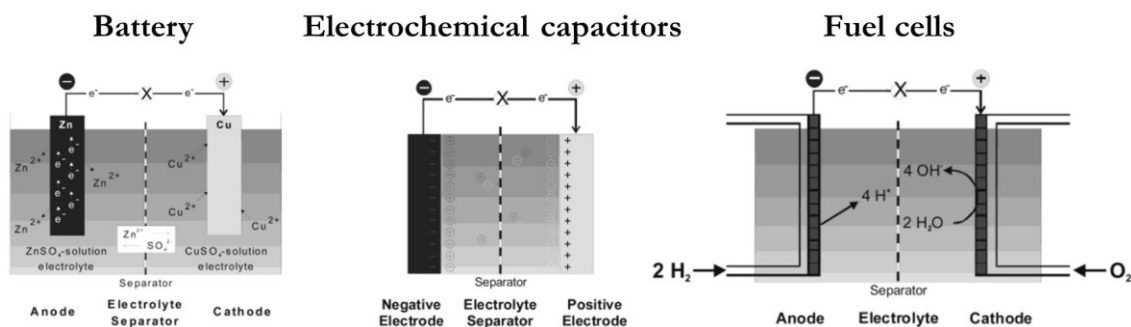


Figure 1-6 Schematic representations of commonly used electrical energy devices [26]

ECs, batteries, and fuel cells all consist of similar components: two active electrodes separated with an insulating separator that allows conduction of ions but inhibits conduction of electrons (Figure 1-6). [26] In fuel cells, differently, there is a constant flow of reactants (H_2 and O_2 as the primary). The operating cell potential is limited by the decomposition of solvent used: aqueous electrolytes work in around 1.0 V, whereas use of organic ones increases the range up to 3.5 V.

1.2.1. Electrochemical Capacitors

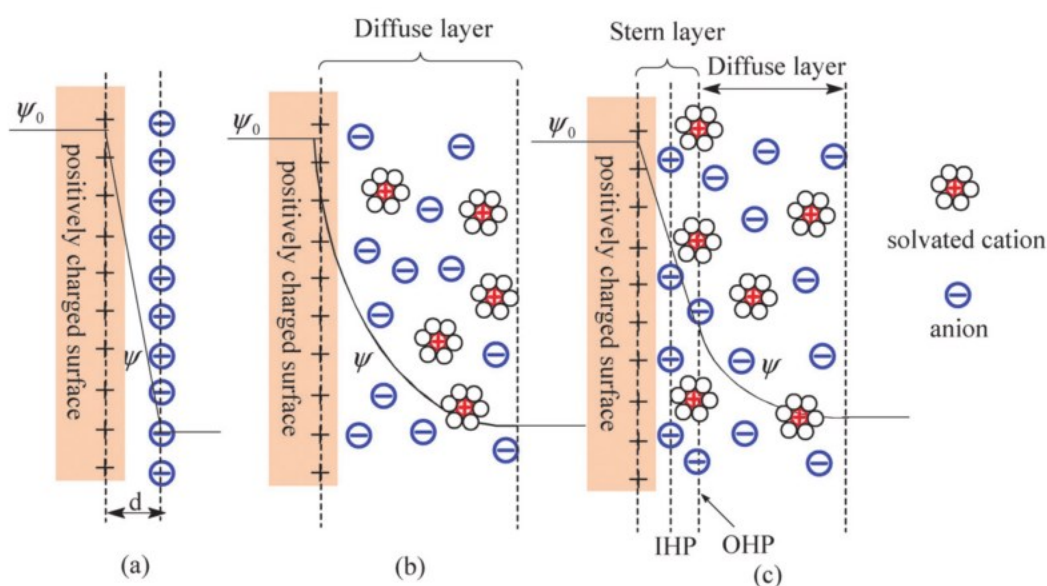


Figure 1-7 Models of double-layer formed when a positively charged electrode comes into contact with electrolyte (a) the Helmholtz model (b) the Gouy-Chapman model (c) the Stern model including inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP) [30]

Electrochemical capacitors (ECs), also known as supercapacitors, are simply capacitors that work in a liquid environment. When a polarized electrode is immersed in an electrolyte, a double layer forms immediately consisting of ions oppositely charged to the metal (Figure 1-7). The formation of the double layer is modelled by Helmholtz in the 19th century; oppositely charged layers (electrode and electrolyte) are separated by an atomic distance. [27] After 60 years of Helmholtz's report, the model was modified by Gouy and Chapman with the consideration of continuous distribution of cations and anions rather than one compact double layer. [28,29] The motion of the ions is induced thermally, creating a diffuse layer near the electrode. In 1924, Stern combined

the studies of Helmholtz, Gouy, and Chapman; creating a model that is widely recognized until this day. The region near the electrode is divided into two; the Stern layer (compact layer) is composed of strongly adsorbed ions (generally anions irrespective of electrode charge) and non-specifically adsorbed counterions, the diffuse layer is similar to what Gouy-Chapman model states. [30]

1.2.1.1. Electrical Double Layer Capacitors

ECs are commonly categorized into two: electrical double layer capacitors (EDLCs) and pseudocapacitors. The capacitance of EDL (C_{dl}) is defined as:

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \quad (1-3)$$

where C_H is the compact double layer capacitance and C_{diff} is the diffuse-layer capacitance. Overall, C_{dl} can be expressed as:

$$C_{dl} = \frac{Q}{V} = \frac{\epsilon_r \epsilon_0 A}{d} \quad (1-4)$$

where Q is the total charge accumulated at the potential V , ϵ_r is the dielectric constant of the electrolyte, ϵ_0 is the dielectric constant of vacuum, d is the distance between charges, and A is the surface area of electrode. [31] According to the above equation, C_{dl} is directly proportional to the surface area of electrode, and inversely to the charge separation. In this regard, C_{dl} of EDLCs are much larger than that of dielectric capacitors since distance between charges is in the range of 2-10 Å whereas d of dielectric capacitors is in the order of μm .

In EDLCs, charge is stored via adsorption/desorption of cations/anions at the electrode/electrolyte interface without any faradaic reactions. As electrode materials, carbon derivatives are commonly used due to their high electrical conductivity, high surface area, corrosion resistance, low cost, and high compatibility with composite materials. [32] In this regard, utilization of high surface area carbon electrodes with good electrical conductivity is highly desirable.

1.2.1.2. Pseudocapacitors

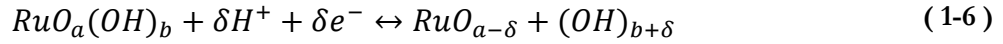
Pseudocapacitors are the second type of ECs; the prefix “pseudo” comes from the Greek combination of “pseudes” (false) and “pseudos” (falsehood). “Pseudo” has two meanings: something that is false or fake, and not actually but having the appearance of. In the field of ECs, use of the second definition of pseudo is more accurate since pseudocapacitors have electrochemical signature of capacitors, but store charge with different mechanisms. [33]

In the Conway’s widely-acknowledged book on ECs, he defines pseudocapacitors as: “*Regular double layer capacitance arises from the potential-dependence of the surface density of charges stored electrostatically (i.e., non-faradaically) at the interfaces of the capacitor electrodes. (...) Pseudocapacitance arises at the electrode surfaces where a completely different charge-storage mechanism applies. It is faradaic in origin, involving the passage of charge across the double layer, as in battery charging or discharging, but capacitance arises in account of the special relation that can originate for thermodynamic reasons between the extent of charge acceptance (Δq) and the change of potential (ΔV), so that the derivative $d(\Delta q)/d(\Delta V)$ or dq/dV , which is equivalent to a capacitance, can be formulated and experimentally measured by dc, ac, or transient techniques. (. . .)*” [34] Overall, pseudocapacitance is classified into three types: underpotential deposition (UPD), surface redox reactions, and intercalation reactions. UPD includes deposition of metal monolayer from cationic solutions onto another metal at potentials lower than thermodynamic potential of reduction:



where M is the deposited metal monolayer, S is the surface of the other metal. If the interaction between S and M is stronger than that of bulk M-M, M can be deposited more easily onto S than onto M electrode, resulting in lower deposition potentials than equilibrium potential of metal reduction ($E_0(M^{z+}/M^0)$). [31] The second pseudocapacitance mechanism includes surface redox reactions typically observed in metal oxides, the most famous one being hydrous ruthenium oxide

(RuO₂.xH₂O). RuO₂ store charge by double injection of electrons and protons, resulting in high specific capacitances of 1300 F g⁻¹ [35]:



The toxicity and high-cost of Ru leads researchers to study different transition metal oxides/hydroxides, generally cheaper ones. MnO₂ is the second widely-studied alternative to RuO₂ followed by iron and cobalt oxides. [36] The surface redox reactions in transition metal oxides are governed by the following reactions of protons or alkali metal cations (C⁺= Li⁺, Na⁺, K⁺, etc.):



Lastly, intercalation pseudocapacitance arises when quasi-2D crystals intercalate/deintercalate cations (Li⁺) without any crystallographic phase change. Most commonly used 2D materials include MoS₂ [37], TiS₂ [38], Nb₂O₅ [39], and metal carbides (MXenes) [40,41]. The charge storage mechanism of intercalation pseudocapacitance is like that of RuO₂; the reaction generally includes double intercalation of electrons and protons/alkali metal cations.

1.2.1.3. Electrochemical Characterization Techniques for the Electrochemical Capacitors

There are several ways to characterize an electrode material as ECs. Cyclic voltammetry (CV), galvanostatic/potentiostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) are the commonly utilized ones.

1.2.1.3.1. Cyclic Voltammetry

CV includes measurement of current response of an electrode while sweeping the potential linearly with time back and forth in the pre-determined voltage range. The measurement is conducted in a 3-electrode or 2-electrode electrochemical cell. In the 3-electrode setup, potential is applied to the electrode of interest (working electrode) with respect to the second electrode (reference electrode). The current is measured simultaneously with the third electrode, the counter (auxiliary)

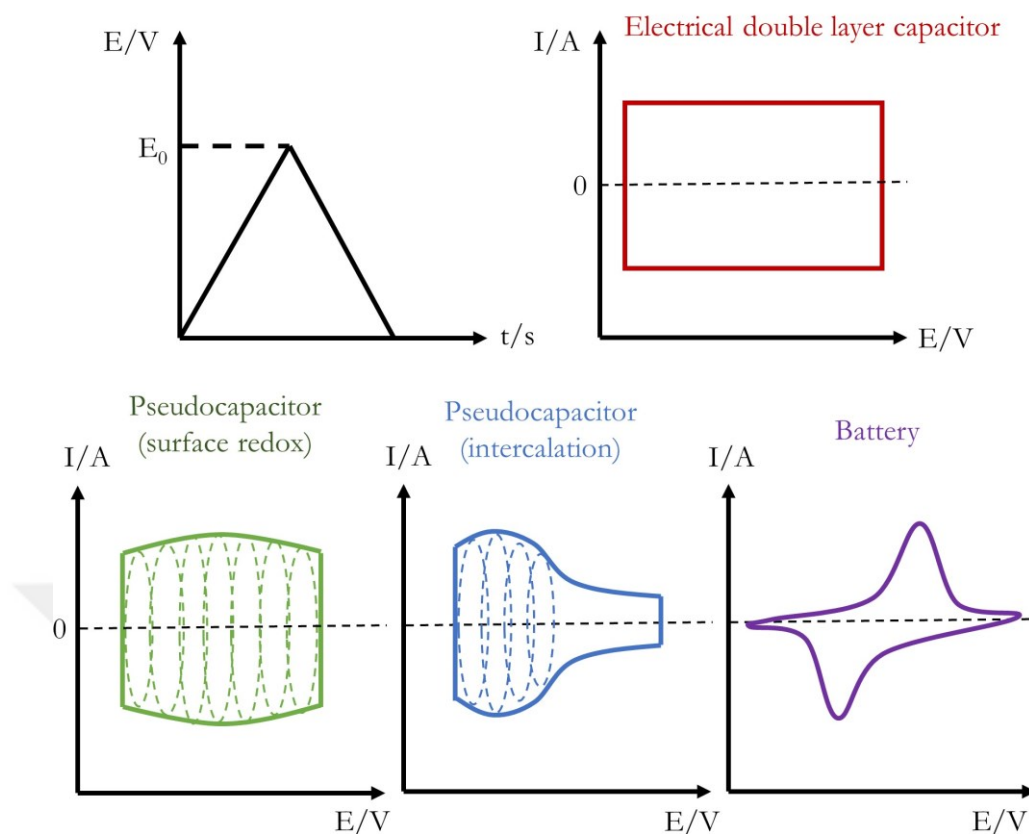


Figure 1-8 Variation of potential with time in CV technique (above), typical cyclic voltammograms of different EC types and batteries (below)

electrode. 2-electrode setup is generally used for the simulation of practical use, where the two electrodes can be of same nature (symmetric ECs), or different (asymmetric ECs). Figure 1-8 demonstrates the change of potential with time in CV measurements and typical cyclic voltammograms of the commonly used energy storage devices. EDLCs exhibit perfect rectangular shape in their working potential range. On the other hand, pseudocapacitors can exhibit either rectangular voltammograms (like in RuO_2 and MnO_2), or rectangular voltammograms distorted with wide anodic and cathodic peaks (bumps) (Figure 1-8). Conversely, in batteries, well-separated anodic and cathodic peaks are observed where the increase in peak separation indicates decrease in reversibility of the system. [42] This irreversibility in batteries lies in the charge storage mechanism: batteries undergo crystallographic phase change during charge-discharge. Another way to differentiate an EC or a battery material is to analyze the variation of shape of the voltammogram with scan rate. As shown in Figure 1-9, in pseudocapacitors, the anodic and

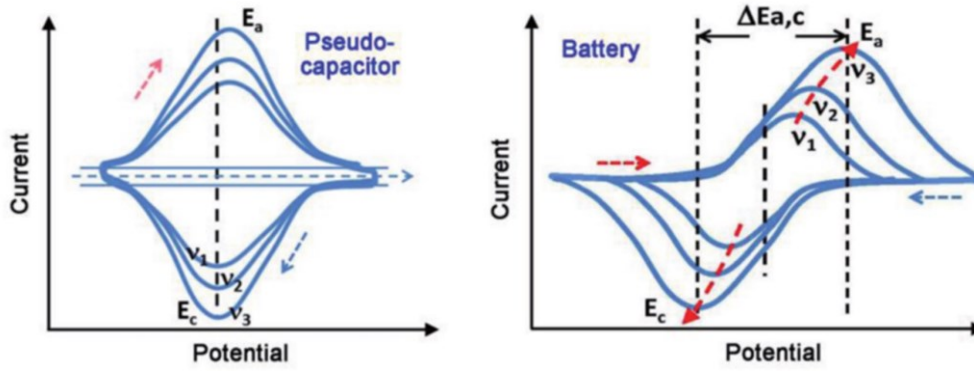


Figure 1-9 Variation of voltammograms with scan rate for pseudocapacitors and batteries [31]

cathodic peaks are not separated with increase in scan rate (until a critical one). Whereas in batteries, peak separation increases with increase in scan rate due to diffusion-related limitations. From the integration of the area enclosed by the cyclic voltammograms, specific (gravimetric) capacitance (SC, F g⁻¹) can be calculated as follows:

$$SC = \frac{Q}{2 \times \Delta V \times m} \quad (1-9)$$

where Q is the voltammetric charge, ΔV is the potential range of measurement, and m is the mass of active material. The factor 2 is placed in the denominator to calculate average capacitance of forward and reverse scan. Thus, the specific capacitance is directly proportional to the area enclosed by the voltammogram.

1.2.1.3.2. Charge-Discharge Measurements

The second widely used technique to evaluate electrochemical performance of energy storage devices is charge-discharge measurement. Charge-discharge can be performed galvanostatically (constant current) or potentiostatically (constant potential). In galvanostatic charge-discharge, a constant current is applied for a certain period (charging), followed by applying the negative current with the same magnitude (discharging). During charge and discharge processes, potential change is measured with time (Figure 1-10). The specific capacitance can be also calculated from the charge-discharge curves by using the following equation:

$$SC = \frac{I \times \Delta t}{\Delta V \times m} \quad (1-10)$$

where I is the charging or discharging current, Δt is the charge or discharge time observed, ΔV is the potential range of measurement, and m is the mass of active material. With the formula, charge and discharge capacitances are calculated separately, and the average is reported as the average SC. As seen from Figure 1-10, ECs exhibit linear charge-discharge curves accompanied with an IR drop in the beginning of discharge curve. IR drop is caused by the resistance in components of the electrochemical cell. Conversely, batteries have a distinct discharge plateau due to diffusion-limited processes.

The energy and power density of an EC can be calculated by using the following equations:

$$E = \frac{1}{2} CV^2 \quad (1-11)$$

$$P = \frac{V^2}{4R_s} \quad (1-12)$$

where V is the working potential range, R_s is the equivalent series resistance.

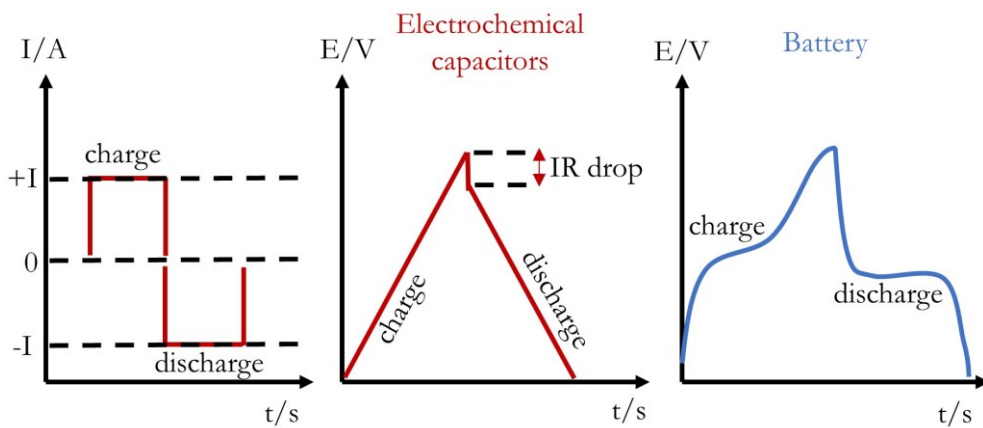


Figure 1-10 Variation of current with time in galvanostatic charge-discharge measurements (left) Typical charge-discharge curves of ECs and batteries (right)

1.2.1.3.3. Electrochemical Impedance Spectroscopy

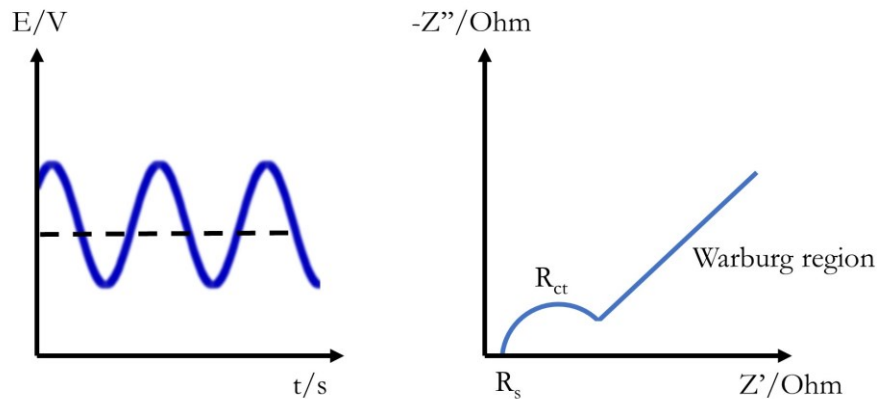


Figure 1-11 Variation of applied potential with time in EIS measurement (left), typical Nyquist diagram of an EC (right)

EIS measures complex resistance of an electrochemical cell. A sinus potential is applied near the equilibrium potential of the system ($E=E_0+E'\cos\omega t$) and the current ($I=I_0+I'\cos(\omega t+\varphi)$) is measured at the same frequency (ω) with a phase delay (φ) (Figure 1-11a). [43] The impedance has a resulting complex definition of $Z=(E'/I')\exp(-i\varphi)$, where i being the imaginary unit. This complex term Z can be divided into real ($Z'=\text{Re}(Z)=(E'/I')\cos\varphi$) and imaginary ($Z''=\text{Im}(Z)=-(E'/I')\sin\varphi$) parts. The plot of imaginary vs real component of impedance is known as the Nyquist plot and used to compare electrochemical systems with different nature. In the Nyquist plot of ECs, a semicircle is observed representing the charge-transfer resistance of fast redox reactions accompanied with straight line with a slope of 45° (Figure 1-11b). The straight line represents Warburg region and is related with the diffusion of electroactive species. The intersection of Nyquist curve to the real axis gives the solution resistance. Fitting of these plots by considering complex equivalent circuits is necessary to calculate cell component parameters. [36] Overall, EIS gives valuable information about resistance of cell components and electrode kinetics.

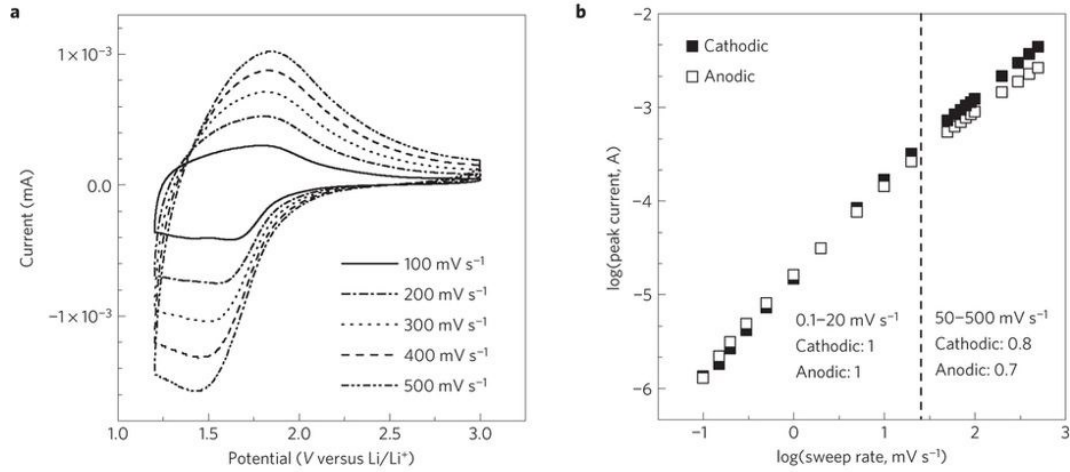


Figure 1-12 (a) Cyclic voltammograms of orthorhombic Nb₂O₅ electrodes at different scan rates (b) variation of peak current with scan rate [39]

1.2.1.3.4. Differentiation of Currents Arising from Capacitive and Diffusion-Limited Processes

The current response in a CV measurement can be written as the sum of currents arising from capacitive (i_{cap}) and diffusion-limited processes (i_{diff}). Capacitive currents originate from double-layer effect or fast faradaic (and reversible) surface reactions, whereas diffusion-limited current arise from crystallographic phase changes. [31]

$$i(\nu) = i_{cap} + i_{diff} = a\nu^b \quad (1-13)$$

$$\log i(\nu) = \log a + b \log \nu \quad (1-14)$$

where ν is the scan rate (mV s^{-1}). Parameter b can be determined by the slope of $\log i(\nu)$ vs $\log \nu$. For capacitive or fast faradaic surface reactions, $b=1$; for batteries or diffusion-limited processes, $b=0.5$. Thus, for EDLCs and pseudocapacitors, current response changes linearly with scan rate. For batteries, current changes linearly with the square-root of scan rate. A b -value in between 0.5 and 1 indicates an electrode in a “transition” range. For instance, the mechanism of Li^+ intercalation on orthorhombic Nb₂O₅ electrode was investigated by Dunn et al. [39]. Cyclic voltammograms exhibited pronounced anodic and cathodic peaks, where the peak positions did not change with increase in scan rate. The analysis of the charge storage mechanism resulted in

calculation of b-value of 1 at lower scan rates, with slight decrease at higher scan rates ($>50 \text{ mV s}^{-1}$) (Figure 1-12).

Quantitative evaluation of currents arising from capacitive and diffusion-limited processes can be performed by modifying equation (1-13):

$$i(V) = i_{cap} + i_{diff} = k_1 v + k_2 v^{\frac{1}{2}} \quad (1-15)$$

which can be rearranged to give:

$$\frac{i(V)}{v^{\frac{1}{2}}} = k_1 v^{\frac{1}{2}} + k_2 \quad (1-16)$$

By plotting $i(V)/v^{\frac{1}{2}}$ vs $v^{\frac{1}{2}}$, k_1 and k_2 can be calculated from the slope and intercept, respectively. Thus, it is possible to distinguish the contributions of capacitive ($k_1 v$) and diffusion-limited ($k_2 v^{\frac{1}{2}}$) processes. [39]

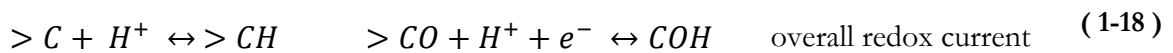
1.2.1.4. Graphene as an Electrochemical Capacitor Electrode

Since the first report on graphene as an EC electrode in 2008 [44], bare graphene and its composites have been exploited for energy storage applications. Table 1-3 compares most commonly used carbon-based electrode materials for energy storage devices. Traditionally,

Table 1-3 Properties of commonly used carbon electrodes for energy storage [45]

Properties	Graphene	Graphite	Activated carbon
Dimension	2D	3D	3D
Specific surface area / $\text{m}^2 \text{g}^{-1}$	~ 1500 (theoretical ~ 2630)	10-20	1500
Electrical conductivity / S cm^{-1}	~ 2000	2-30000	low
Density / g cm^{-3}	0.05-0.75	2.2	0.5-0.7
Theoretical Li^+ storage capacity / mA h g^{-1}	744 (LiC_3)	372 (LiC_6)	-
Theoretical EDL capacitance / F g^{-1}	550	-	150-300

graphite has been used as the Li-ion battery anode and activated carbon has been used as EC electrode. High theoretical surface area and electrical conductivity make graphene an ideal electrode material for ECs. Due to utilization of both surfaces of carbon network, graphene has twice the theoretical Li^+ storage capacity of graphite. When the theoretical surface area of graphene is fully utilized, it has theoretical double-layer capacitance of 550 F g^{-1} . However, there are several reasons that graphene usually does not achieve this high capacitance. First one is the re-stacking of graphene (or reduced GO) sheets during preparation of electrode materials due to van der Waals interactions between the restored graphene sheets. During the re-stacking, graphene loses most of the available surface area that will be otherwise exposed to electrolyte. Second reason is the trade-off between high electrical conductivity and high surface area of graphene electrodes. When the surface area is increases, generally the electrical properties deteriorate due to the presence of large pores and/or defects. For the complete utilization of electrochemical properties of graphene, high surface area graphene electrodes with high electrical conductivity should be produced. Additionally, decorating graphene with defects and electroactive materials (metal oxide/hydroxide) will enhance the pseudocapacitive properties of graphene resulting in high energy-density materials. [45] Addition of electroactive particles can also solve the re-stacking problem by acting as “spacers” between the graphene layers. Moreover, control of oxygen functional groups on the GO layers is crucial in determining the final performance of electrodes. In this regard, Liu and Xue [46] investigated the electrochemical properties of graphene electrodes with controlled surface functionalities (Figure 1-13). They reported pseudocapacitive properties of oxygen functional groups on GO layers, and claimed that the redox peaks observed in CV measurements result from the following reactions:



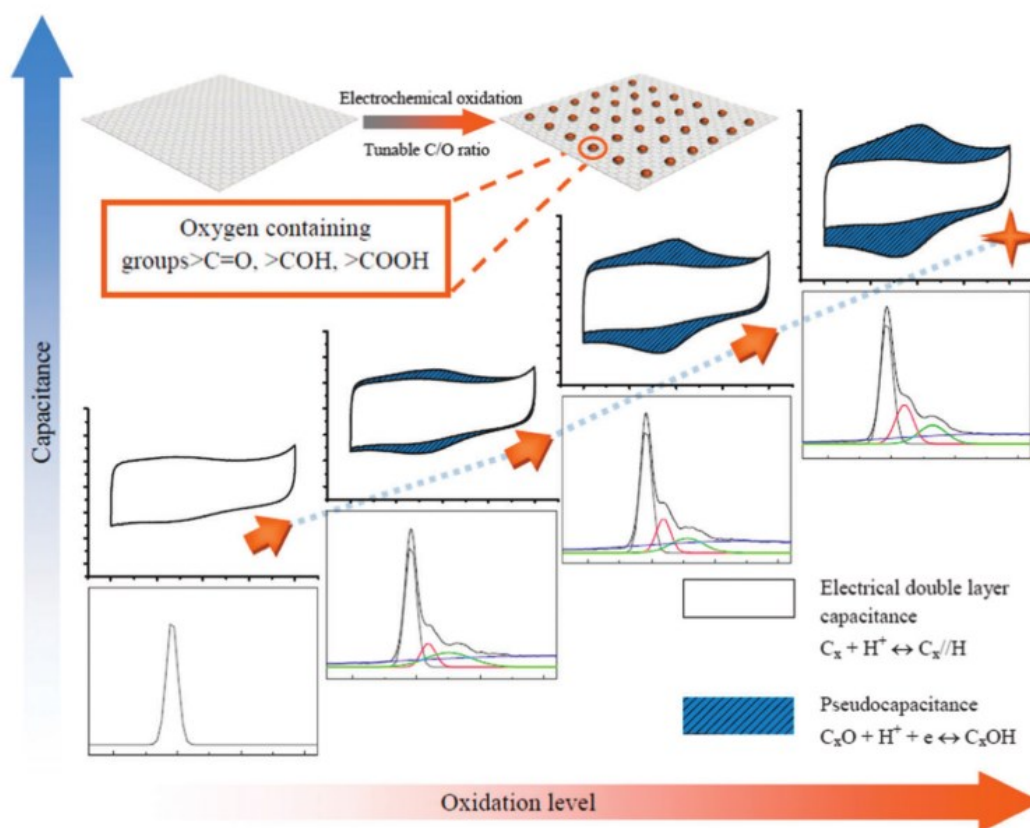


Figure 1-13 Schematic representation of the effect of increasing functional groups of GO on its pseudocapacitance [46]

With the controlled electrochemical oxidation of graphene, the pseudocapacitance arising from oxygen functional groups can be modified. Similar report on pseudocapacitive properties of oxygen functional groups of GO has also been reported previously. [47]

1.2.2. Fuel Cells

As previously mentioned, fuel cells cover the high energy-density region in the Ragone plot among the other energy storage devices. Fuel cells convert chemical energy into electrical one with the continuous supply of reactants (fuels). The schematic representation of the device is given in Figure 1-6 where H_2 is supplied to the anode and O_2 is supplied to the cathode. At the anode, H_2 is oxidized to produce protons (H^+), protons move towards cathode passing through an electrolyte, and meet with O_2 to produce H_2O and some heat. [26] The corresponding reactions of the simple H_2 - O_2 fuel cell are as follows:



The anodic reaction is the hydrogen oxidation reaction (HOR), and the cathodic reaction is the oxygen reduction reaction (ORR). ORR is a two-step reduction with hydrogen peroxide (H_2O_2) as the intermediate product. The stability of this intermediate is generally undesirable since H_2O_2 can be detrimental to the electrode materials which are composed of carbon. The fuels of $\text{H}_2\text{-O}_2$ cell, H_2 and O_2 , can be produced by simple water electrolysis cell or a solar water-splitting device. The anodic reaction of the electrolysis cell is the oxygen evolution reaction (OER), and the cathodic one is the hydrogen evolution reaction (HER). Overall, four fundamental reactions that governs the simple fuel cell technology is presented in Figure 1-14. [48] The standard reduction potentials of HOR and HER are at 0.00 V vs SHE which is the reference redox reaction in determination of standard reduction potentials. The standard potential for the hydrogen involving reactions are pH dependent due to involvement of H^+ in the reaction and decreases by 59.2 mV per unit increase

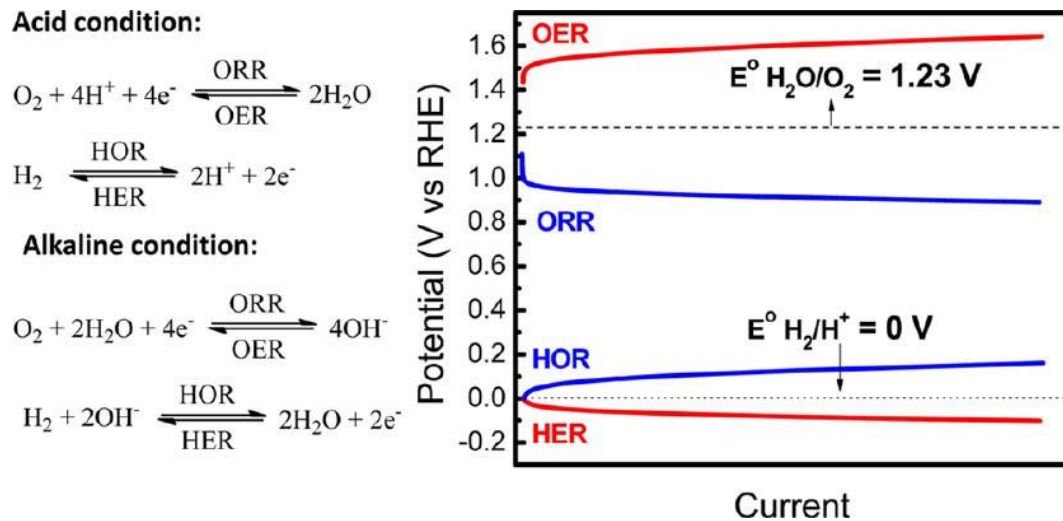


Figure 1-14 The four fundamental reactions involving hydrogen and oxygen electrochemistry and their corresponding polarization curves [48]

in pH. To prevent confusion in the overall pH range, reversible hydrogen electrode (RHE) is generally preferred which operates pH-independent and has a fixed potential of H^+/H_2 redox couple at 0.00 V. Furthermore, O_2/H_2O redox couple has a standard potential of 1.23 V vs RHE (Figure 1-14). In short, the relationship between RHE and SHE can be expressed as:

$$E_{RHE} = E_{SHE} + 0.0592 \times pH \quad (1-23)$$

1.2.2.1. Electrode Kinetics

In terms of reaction kinetics, the current density (j) observed for an electrochemical reaction can be expressed by the well-known Butler-Volmer equation [43]:

$$j = j_0 \left[\exp\left(\frac{\alpha_a n F \eta}{RT}\right) - \exp\left(-\frac{\alpha_c n F \eta}{RT}\right) \right] \quad (1-24)$$

j_0 is the exchange current density where anodic and cathodic reactions are in equilibrium, α_a and α_c are anodic and cathodic transfer coefficients, F is the Faraday constant, R is the universal gas constant, T is temperature, and η is the overpotential ($\eta = E - E_0$). Overpotential is the difference between the real (observed) potential and the standard equilibrium potential of a redox reaction (Figure 1-15).

For large overpotentials to either side of reaction, the Butler-Volmer equation splits into two individual anodic and cathodic current densities (j_a and j_c , respectively) [49]:

$$j_a = j_0 \exp\left(\frac{\alpha_a n F \eta_a}{RT}\right) \quad (1-25)$$

$$j_c = -j_0 \exp\left(-\frac{\alpha_c n F \eta_c}{RT}\right) \quad (1-26)$$

These current density equations can be converted to overpotential expressions:

$$\eta_a = \frac{RT}{\alpha_a n F} \ln j - \frac{2.3RT}{\alpha_a n F} \ln j_0 = b \ln j - a \quad (1-27)$$

$$\eta_c = \frac{RT}{\alpha_c n F} \ln j_0 - \frac{2.3RT}{\alpha_c n F} \ln j = a - b \ln j \quad (1-28)$$

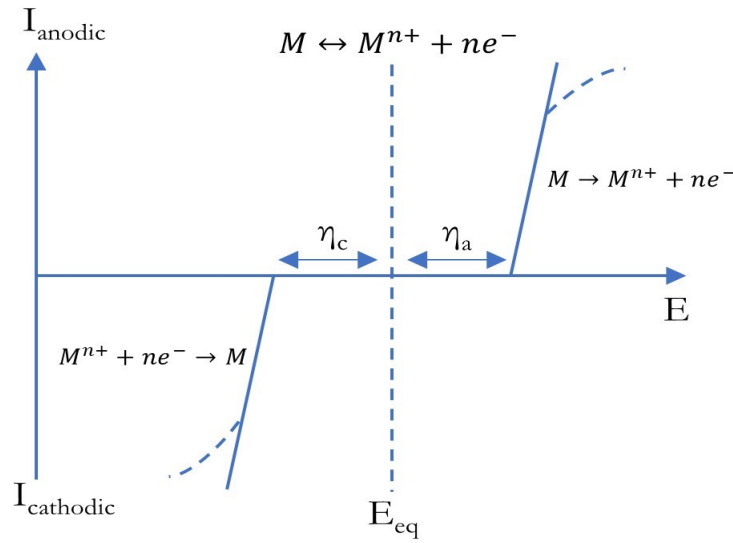


Figure 1-15 Current-potential response of an electrochemical reaction which requires overpotentials for anodic (η_a) and cathodic (η_c) processes. E_{eq} is the standard equilibrium potential of the reaction. Dashed curves represent control of the reaction rates by mass-transfer.

which are known as the Tafel relations. Thus, the Tafel relation gives valuable information about the relationship between current density and overpotential. Plot of η vs $\log j$ are known as Tafel plots which have slopes of b ; $2.3RT/\alpha nF$ for the cathodic and $2.3RT/(1-\alpha)nF$ for the anodic process (Figure 1-16). The experimental Tafel plots do not cut the $\log j$ axis; the extrapolated asymptotes intersect on the line $\eta=0$ at $\log j_0$, where j_0 is the exchange current density. [50] Higher exchange current density (j_0) and smaller Tafel slopes mean that higher currents can be attained by applying low overpotentials. Thus, activation of reaction is easier resulting in faster electrode kinetics. [51] The magnitude of overpotential is determined by three individual contributions:

$$\eta = \eta_A + \eta_C + \eta_R \quad (1-29)$$

where η_A is the activation overpotential, η_C is the concentration overpotential, and η_R is the resistance overpotential. η_A is related to the activation energy of the electrochemical reaction; slow or sluggish reactions require higher activation potentials to cross the energy barrier. The second type, η_C is related to the concentration gradient between near electrode and the bulk solution; mass

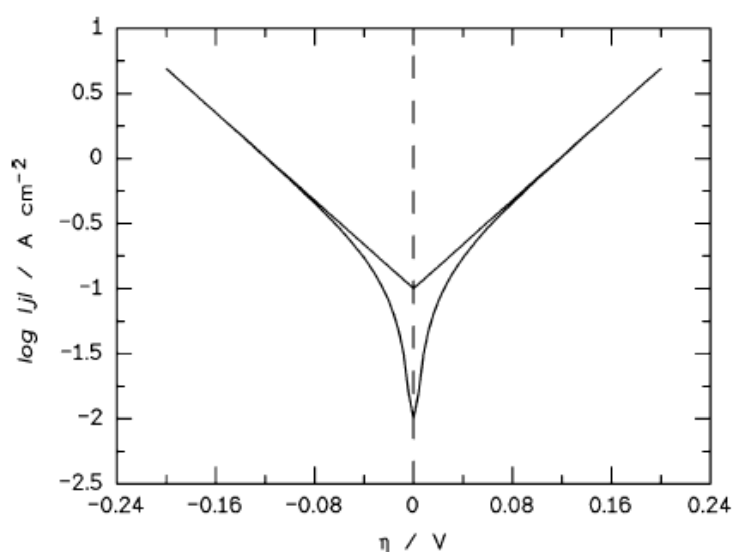


Figure 1-16 An example of Tafel plot assuming $\alpha=0.5$ and $j_0= 0.1 \text{ A cm}^{-2}$ [43]

transport effects determine the magnitude of η_C . The third type, η_R results from the resistance of all the components of the electrochemical cell: electrode connections (cables), electrode-electrolyte interface, and electrolyte solution. Overall, all the afore-mentioned processes occur simultaneously and lower the potential of an electrochemical cell ($E_{\text{cell}} = E^0 - \eta_A - \eta_C - \eta_R$). [26,50]

As seen from Figure 1-17, while HER and OER obeys Butler-Volmer model even at high overpotentials, currents of HOR and ORR reaches a limiting value due to mass transfer limitations. There are three types of mass transfer occurring in the electrochemical cells: migration, diffusion, and convection. Migration is the movement of anions/cations in the electrolyte by the applied potential on the electrodes. Diffusion is the movement of species from higher to lower concentration; this is caused by the depletion of species that are being reduced/oxidized near the electrode surface. Convection, on the other hand, results from external effects like stirring, vibration, shock, or temperature gradients. [50]

Among the hydrogen and oxygen-involving electrochemical processes, two-electron transfer including HER and HOR are straightforward in terms of reaction kinetics, whereas multistep OER and ORR are sluggish. [51] In this regard, design of efficient electrocatalysts for both OER and ORR is of utmost importance and determines the final performance of fuel cells.

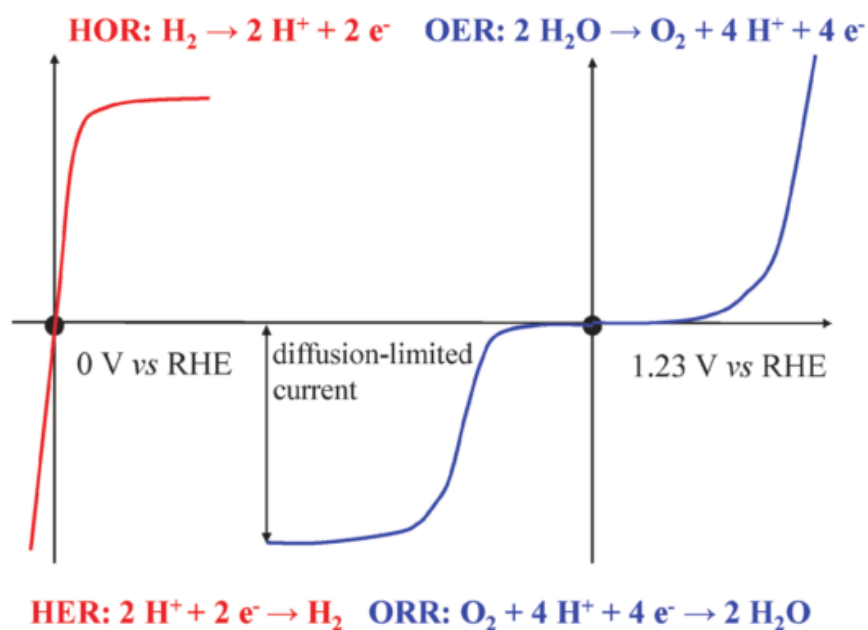


Figure 1-17 Polarization curves of the main electrochemical reactions of hydrogen (red curve) and oxygen (blue curve). The lines are not drawn to scale. [51]

1.2.2.2. Oxygen Evolution Reaction

OER is the oxidation of H_2O or OH^- to molecular oxygen (O_2) depending on the reaction medium. The exact mechanism of OER is highly dependent on the electrode surface; different catalysts or different crystal planes on one material can follow various reaction routes. Nevertheless, widely-accepted OER mechanism is the four electron pathway, which is tabulated in Table 1-4 for both acidic and alkaline electrolytes. [51] In acidic solution, water oxidation to O_2 has standard potential of 1.229 V vs SHE. In basic solution, hydroxyl oxidation to O_2 and H_2O has standard potential of 0.401 V vs SHE. Thus, thermodynamically, OER is more favorable in alkaline solutions. If these potentials are reported vs RHE, they would have the same potential value (1.229 V). The performance of electrocatalysts used for OER lowers substantially as the pH is decreased. [52]

As catalysts, the most active materials are noble metals, in acidic solutions the activity follows the order: $\text{Ru} > \text{Ir} > \text{Pd} > \text{Rh} > \text{Pt}$. The stability of the electrocatalyst is determined by the formation of oxide layer on the surface of metal and the activity trend is reversed for the stability; Pt is the most stable and Ru is the least stable in OER measurements. [51] In general, rutile type RuO_2 has

the highest activity in all pH range. [53] The second most widely used class of materials is transition metal (oxides): Ni- and Co- based oxides, mixed oxides like spinel-type or perovskites, and large number of molecular catalysts. [51]

Table 1-4 Overall reaction pathways for OER in acidic and alkaline media

Electrolyte	Overall reaction (medium)	Reaction pathway
Acidic	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$* + H_2O \rightarrow *OH + H^+ + e^-$ $*OH \rightarrow *O + H^+ + e^-$ $*O + H_2O \rightarrow *OOH + H^+ + e^-$ $*OOH \rightarrow *O_2 + H^+ + e^-$ $*O_2 \rightarrow * + O_2$
Alkaline	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	$* + OH^- \rightarrow *OH + e^-$ $*OH + OH^- \rightarrow *O + H_2O + e^-$ $*O + OH^- \rightarrow *OOH + e^-$ $*OOH + OH^- \rightarrow *O_2 + H_2O + e^-$ $*O_2 \rightarrow * + O_2$

* represents catalytic active site

For the comparison of activities of the electrocatalysts, plots of j_0 vs $\Delta G_{\max}$ are very useful which are found out to be of volcano-type. Figure 1-18a present Volcano plot for HER where x axis is the ΔG for binding of H to the catalytic active site (*). According to Volcano plots, optimal catalytic activity can be obtained by appropriate binding energies of reactants to the catalytic active sites. In this regard, if the reactants bind the surface too weakly, the activation is difficult; if they bind too strongly, all the active sites will be occupied (Sabatier principle). [54] The basis for the construction of Volcano plot for OER is pioneered by Trasatti [55], who demonstrated that the catalytic activity of metal oxides towards OER is related with the enthalpy of transition of increasing the valence of metal oxides. In this regard, metal oxides that can oxidize harder have low activity since the reaction intermediates are weakly adsorbed, and water dissociation becomes the rate-determining step. Conversely, metal oxides that can easily oxidize exhibits also low activity;

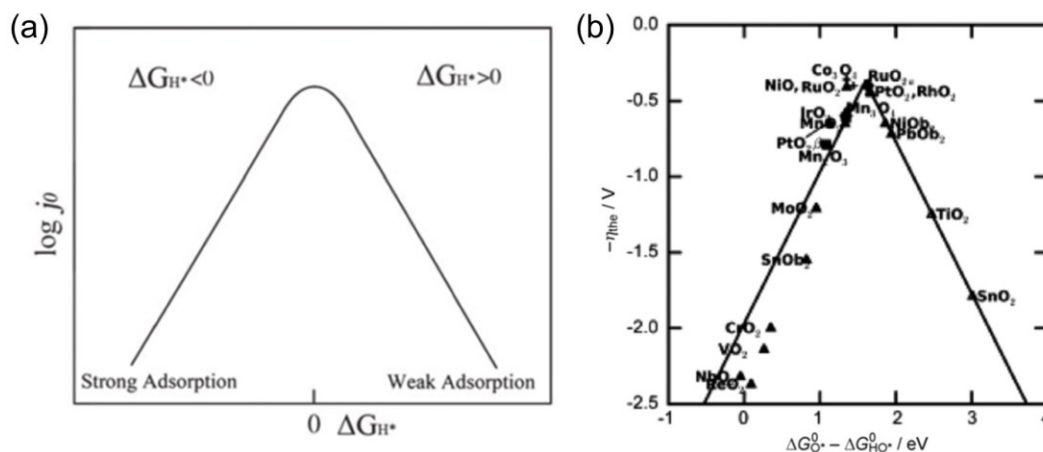


Figure 1-18 (a) Volcano plot (b) Activity of various catalysts for OER as a function of $\Delta G_{O^*} - \Delta G_{OH^*}$ [51]

reaction intermediates bind too strongly, and desorption of oxygenated species become the rate-determining step. Later, the activity was related with a single descriptor ($\Delta G_{O^*} - \Delta G_{OH^*}$) which resulted in the construction of Volcano plot for OER (Figure 1-18b). [55]

The binding strength between reaction intermediates and catalysts provide useful information in determining the activity, albeit not enough to predict the activity of new materials. In this regard, there has been a significant effort on correlating the binding strength of reaction intermediates and the electronic band structure of metals/alloys. [56–59] Specifically, the d-band model correlates the position of the Fermi level (ϵ_F) with the surface reactivity. The binding energy of an adsorbate onto a surface depends on the electronic structure of the surface (metal). For instance, binding of an oxygen-containing species to a transition metal results in formation of filled bonding orbital and a partially-filled anti-bonding orbital. The degree of filling of the anti-bonding orbital determines the strength of the resulting metal-oxygen bond. [60]

1.2.2.2.1. Activity Measurements of OER Electrocatalysts

For the activity determination of electrocatalysts towards OER, linear sweep voltammetry (LSV) and rotating disk electrode measurements (RDE) are widely utilized. Prior to LSV measurements, the electrolyte (acidic or basic) is saturated by pure oxygen (O_2) gas by continuous purging with a constant flow rate. Having an O_2 -saturated electrolyte ensures that any produced current is caused

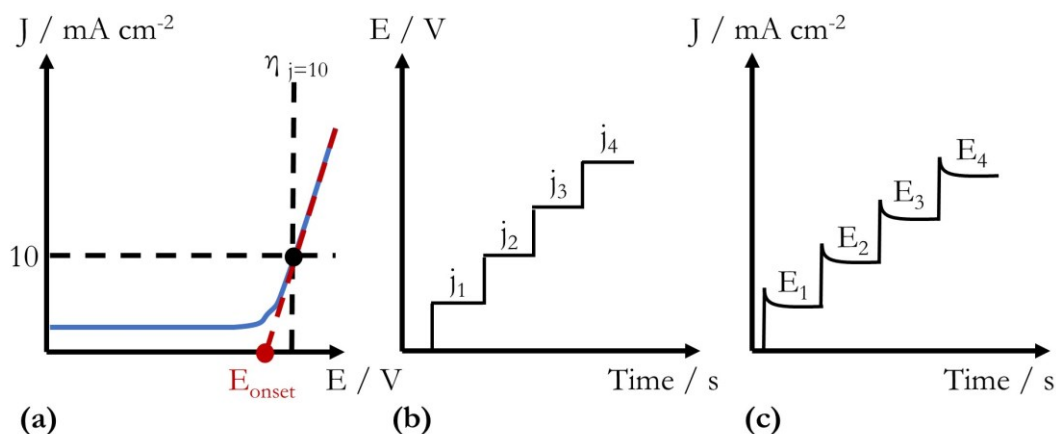


Figure 1-19 (a) Typical OER polarization curve (b) Chronopotentiometric steps (c) Chronoamperometric steps

by the formation of new O_2 , analogous to the measurement of dark current while performing photocatalytic experiments. LSV is performed in a 3-electrode electrochemical cell consisting of reference, counter, and working electrodes. The working electrode loaded with the catalyst is scanned from a potential smaller than 1.23 V (vs RHE) to a potential where an exponential increase in current is observed. The potential at which 10 mA cm^{-2} current density is observed is the point where different catalysts are generally compared. The difference between this potential and the thermodynamic potential of oxygen evolution (1.23 V vs RHE) is called the overpotential at 10 mA cm^{-2} ($\eta_{j=10}$). This current density is chosen since it is the value expected from a 10% efficient solar-water splitting device. The point where the linear fit of OER curve intersects the potential is called the “onset potential (E_{onset})” and determines the lowest potential where the first activity is observed (Figure 1-19a). The positive (or anodic) sweep towards the highest potential is called “OER polarization curve” and generally the reverse sweep is not reported. There are also two other techniques that are complementary to the sweep voltammetry: chronopotentiometric (constant current) and chronoamperometric (constant potential) steps. Chronopotentiometric steps include applying specific current densities ranging from low (0.1 mA cm^{-2}) to high (20 mA cm^{-2}) current densities for certain periods of time (20-30 s) and measuring the potential. Then, overpotentials required to obtain specific current densities can be measured (Figure 1-19b).

Chronoamperometric steps are exactly the reverse of chronopotentiometric measurement (Figure 1-19c).

1.2.2.2.1.1. Hydrodynamic Voltammetry: The Rotating Disk Electrode

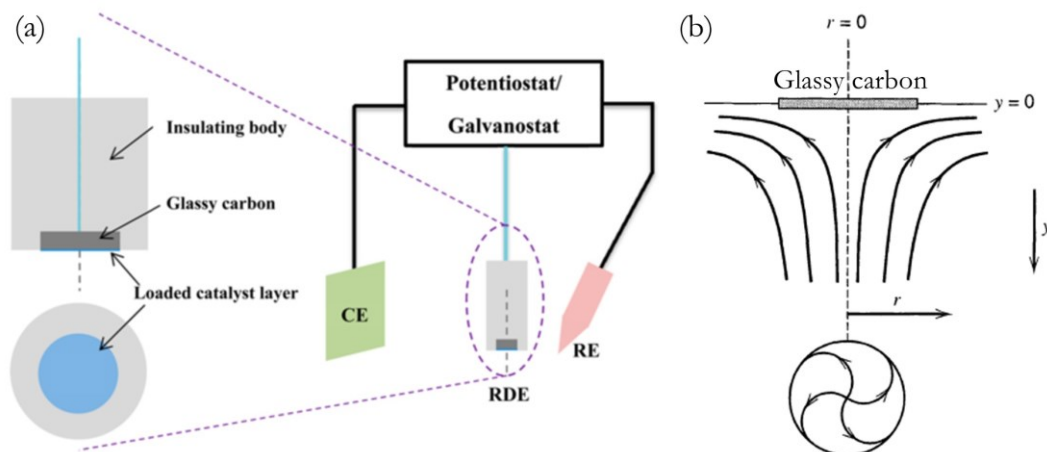


Figure 1-20 (a) Experimental setup for the RDE measurement (b) Schematic representation of the produced streamlines with the rotation of RDE [42,49]

In general, for the investigation of kinetic properties of catalysts and/or eliminate the produced gaseous products (like O_2 and H_2), controlled convection is utilized. Any measurement where controlled convection is used, with the aid of rotation or stirring, is classified under “hydrodynamic voltammetry”. The two most widely-used electrodes in that sense are the rotating disk electrode (RDE) and RRDE (rotating ring disk electrode).

The typical experimental setup used for RDE measurements is presented in Figure 1-20a where RDE is connected to the potentiostat as the working electrode in which the rotor is controlled with another external power (Figure 1-20a). Commonly used RDE includes a cylindrical metal surrounded by an insulating body which rotates in the vertical axis. The rotation of the electrode drags the electrolyte with it and creates a centrifugal force which forces the electrolyte to move outward in a radial direction. As a result, the electrolyte near RDE is replenished by the movement of fluid normal to the surface of the electrode (Figure 1-20b). [42] After reaching equilibrium at constant rotation speed, a diffusion layer forms near the surface since the flux at the electrode

surface is not equal to the mass transfer in the bulk. The thickness of this diffusion layer (δ) is defined as [50]:

$$\delta = \frac{1.62D^{1/3}\nu^{1/6}}{\omega^{1/2}} \quad (1-30)$$

where D is the diffusion coefficient, ν is the viscosity of the electrolyte, ω is the rotation speed.

Overall, polarization and stepwise measurements for OER are conducted during constant rotation of RDE, generally at 1600 rpm. For the polarization curves, a relatively low scan rate is chosen such as 10 mV s⁻¹. The stability tests of OER electrocatalysts are conducted either by chronopotentiometric measurement at 10 mA cm⁻² or chronoamperometric measurements at a specific overpotential (350 mV). Polarization curves of electrocatalysts are compared before and after the stability test to evaluate the change in the overpotential values.

On the other hand, RRDE consists of an additional disc that is separated from the central electrode by an insulating material. This system is utilized for the detection of unstable products formed during the reaction of interest.

1.2.2.2.2. Graphene as Support Material for OER Electrocatalysts

Carbon derivatives are generally prone to electrochemical oxidation when they are used as support for OER electrocatalysts. C can oxidize to CO₂ above +0.207 V vs RHE, but the reaction is kinetically limited below +1.2 V vs RHE. [61] Since OER takes place far above 1.2 V with the need for overpotentials, conventional carbon materials are undesirable as support materials. Alternatively, advanced carbon materials such as CNTs and graphene can be utilized as supports due to their higher electrochemical stability. In this regard, graphene is promising with its excellent electrical conductivity, high specific surface area, and ease of surface functionalization. Graphene derived from chemical oxidation (rGO) can boost OER activity of catalyst in several aspects. First one is the enhanced electron transfer from support to catalyst with high electrical conductivity. It also provides anchoring sites for metals and metal oxides which results in formation of small and stable nanoparticles that are resistant to agglomeration. Furthermore, O or N atoms attached to C

causes formation of positively charged neighboring C atom which then electrostatically attract OH⁻ and H₂O molecules. Consequently, the electron transfer between surface and reaction intermediates like O²⁻ and O₂²⁻ is enhanced, resulting in higher OER activity. [62]

1.2.2.3. Oxygen Reduction Reaction

Table 1-5 Overall reaction pathways for ORR in acidic and alkaline media

Electrolyte	Overall reaction (medium)	Reaction pathway (only 4e ⁻ pathway is given)
Acidic	<u>4 e⁻ pathway:</u> $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ <u>2 e⁻ pathway</u> $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	$* + O_2 \rightarrow * O_2$ $* O_2 + H^+ + e^- \rightarrow * OOH$ $OOH * + H^+ + e^- \rightarrow * O + H_2O$ $* O + H^+ + e^- \rightarrow * OH$ $* OH + H^+ + e^- \rightarrow * + H_2O$
Alkaline	<u>4 e⁻ pathway:</u> $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ <u>2 e⁻ pathway</u> $O_2 + H_2O + 2e^- \rightarrow OOH^- + OH^-$ $OOH^- + H_2O + 2e^- \rightarrow 3OH^-$	$* + O_2 \rightarrow * O_2$ $* O_2 + H_2O + e^- \rightarrow * OOH + OH^-$ $* OOH + e^- \rightarrow * O + OH^-$ $* O + H_2O + e^- \rightarrow * OH + OH^-$ $* OH + e^- \rightarrow * + OH^-$

* represents catalytic active site

ORR is the reverse reaction of OER: O₂ is reduced to form water (acidic electrolyte) or hydroxide (basic electrolyte). The reaction can proceed in either direct 4 e⁻ process or two-step 2 e⁻ process (Table 1-5). Direct 4 e⁻ pathway is highly desirable in fuel cells for high efficiency, and 2 e⁻ pathway is utilized in commercial production of the reaction intermediate, which is a valuable industrial product, hydrogen peroxide (H₂O₂). Analogous to OER, O₂ reduction to form water in acidic solutions has standard reduction potential of 1.229 V (vs SHE), and O₂ reduction to form hydroxide ions in basic solutions has standard potential of 0.401 V (vs SHE). Thus, ORR is more favorable in alkaline solutions thermodynamically.

The Volcano plot for the ORR electrocatalysts is shown in Figure 1-21. The reaction is limited by either formation of OOH^{ads} or removal of OH^{ads}, which means that there should be an

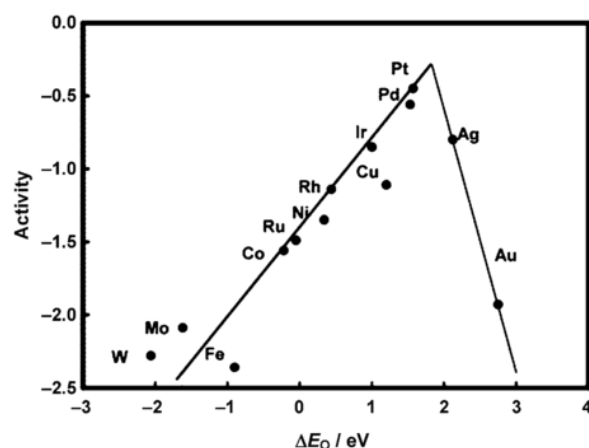


Figure 1-21 Volcano plot for the ORR electrocatalysts [51]

intermediate binding energy of catalyst to oxygen for optimal activity. [63] Among all the metals listed, Pt is located on top of the Volcano plot, which is the commercial catalyst used for ORR. The reaction pathway (2 or 4 e^-) followed is highly dependent on the nature of the catalyst used. While Pt generally prefers direct 4 e^- route, Au and Hg follows two step 2 e^- route. [64] Thus, Pt and its alloy with various metals are widely studied as ORR electrocatalysts. The size, shape, and crystallinity are all found to be determinant in the final activity and stability of Pt catalysts towards ORR. [64] Apart from Pt and Pt alloys, there are other materials utilized as ORR electrocatalysts. Non-noble metals like metal- N_4 organometallic complexes ($M=Co, Fe$), metals supported on nitrogen containing carbon materials ($M-N_x/C$, where $M=Co, Ni, Fe, Mn$), and non-metallic materials such as carbon and nitride-based compounds are among the reported catalysts. [65,66]

1.2.2.3.1. Activity Measurements of ORR Electrocatalysts

Activity measurements of the ORR electrocatalysts are conducted by similar methods with that of OER; CV and RDE techniques are utilized for the calculation of electrochemical surface area (ESA), specific activity, and mass activity.

First, catalyst loaded working electrode is scanned in a 3-electrode cell in N_2 -saturated electrolyte. Specifically, Pt electrocatalysts in acidic electrolyte exhibit H^+ adsorption-desorption peaks, and

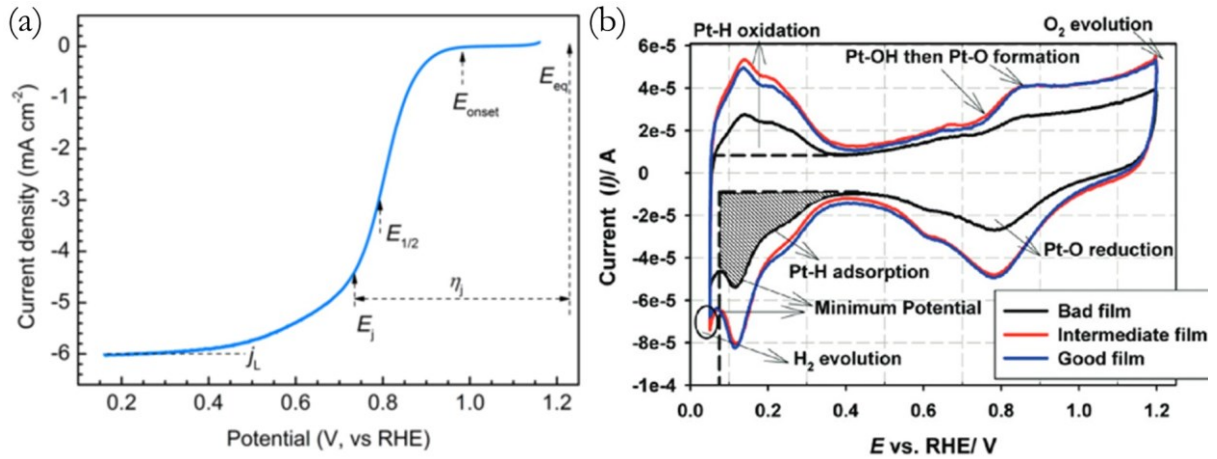


Figure 1-22 (a) Typical ORR polarization curve of an electrocatalyst with rotation rate of 2000 rpm (b) Typical cyclic voltammogram of an ORR electrocatalyst in N_2 -saturated 0.1 M $HClO_4$ [49,67]

redox peaks of Pt/Pt-O transition (Figure 1-22b). Integration of the H^+ adsorption region (excluding the capacitive current) results in calculation of ESA of the metal by the following equation:

$$ESA(m^2 g^{-1}) = \frac{Q_{H-adsorption}(C)}{210 \mu C cm_{Pt}^{-2} L_{Pt}(mg_{Pt} cm^{-2}) A(cm^2)} \times 10^5 \quad (1-31)$$

Where $Q_{H-adsorption}$ is the area of H^+ adsorption region (Figure 1-22b), $210 \mu C cm^{-2}$ is the charge of full coverage for clean polycrystalline Pt and used as a correction factor, L_{Pt} is the Pt loading per unit area, and A is the geometric area of the electrode. [67]

After determination of ESA by CV measurement, the purging gas is switched to O_2 for the activity measurements. ORR polarization curves are recorded in a relatively low scan rate ($5-10 mV s^{-1}$) with a constant rotation speed of RDE (Figure 1-22a). As seen in Figure 1-22a, the polarization consists of two different regions: diffusion-limited current density (j_L) plateau below 0.4 V, and mixed kinetic-diffusion limited region between 0.75 and 0.9 V. The half-wave potential ($E_{1/2}$) is crucial in determination of ORR activity; the more positive the $E_{1/2}$, the higher activity the catalyst has. Overpotentials (η_i) for obtaining specific current densities (E_i) can be also calculated from the

same polarization curve. At the rotation speed of ω , the limiting current density (j_L) is defined by the Levich equation:

$$j_L = 0.62nFD^{2/3}\omega^{1/2}\nu^{-1/6}C_0 \quad (1-32)$$

Where F is Faraday constant, n is the number of electrons transferred, C_0 is the bulk concentration of the active species. The relation between the measured current density and the limiting current density leads to the calculation of mass-transfer corrected kinetic current densities (j_k):

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_k} = \frac{1}{0.62nFD^{2/3}\omega^{1/2}\nu^{-1/6}C_0} + \frac{1}{nFkC_0} \quad (1-33)$$

Equation (1-33) is known as the Koutecky-Levich (K-L) equation where k is the electron transfer rate constant. Thus, plot of $1/j$ vs $1/\omega^{1/2}$ (K-L plots) at different rotation speeds yields calculation of the kinetic current density (j_k) at infinite rotation speed ($1/\omega=0$). The specific activity is simply equal to the kinetic current density, whereas mass activity is calculated by dividing specific activity to the mass of catalyst.

1.2.2.3.2. Graphene as Support Material for ORR Electrocatalysts

For enhancing the activity of ORR electrocatalysts, nanoparticles dispersed onto a high surface area support is highly desirable. As support materials, carbon derivatives are generally used due to their high specific surface area, electrical conductivity, and (electro)chemical stability. [64] Carbon blacks are utilized commercially as Pt catalyst supports, but the absence of surface functionalities causes weakening of metal-support interaction and agglomeration of nanoparticles. Compared to carbon black derivatives, CNTs and graphene have attracted interest due to their high electrical conductivity and mechanical strength, along with their electrochemical stability. [68]

Kou et al. [69] reported enhanced electrocatalytic activity of functionalized graphene sheets (FGS) supported Pt nanoparticles by impregnation method. Produced catalysts exhibit higher ESA, activity, and stability than that of commercial E-TEK catalyst (20 wt% Pt/Vulcan XC-72 Carbon) due to the stability of well-dispersed small (2 nm) Pt nanoparticles on FGS. Apart from being an

ideal support material to noble/non-noble catalysts, heteroatom doped graphene is also utilized as metal-free ORR electrocatalyst. Qu et al. [70] synthesized nitrogen-doped (N-doped) graphene via CVD from methane and ammonia. Produced electrocatalyst showed higher activity and stability than commercial E-TEK catalyst in alkaline medium. Aforementioned studies demonstrate that graphene is a promising material in ORR research field, both as a metal-free catalyst and support material.

1.3. Thesis Overview

This thesis is devoted the synthesis of two and three-dimensional composites of metal and metal hydr(oxide) with graphene derived from reduction of graphene oxide. Produced composites' structural characterization is demonstrated in detail for the understanding of electrochemical properties. Chapter 2 and 3 deal with the electrochemical properties of two-dimensional metal/GO composites, whereas Chapter 4, 5, and 6 introduce electrochemical properties of the next generation three-dimensional form of graphene, graphene aerogels, with or without metal nanoparticles. The following sections summarizes the major aspects of the corresponding chapters.

1.3.1. Electrochemical Properties of Transition Metal/Graphene Oxide Composites

In Chapter 2, composites of first-row transition metals (Co, Ni, Mn, Fe) are combined with GO via simple electrostatic interaction. The nature of interaction between the individual metal and GO layers is investigated by means of mass spectroscopic measurements. Facile electrochemical reduction is performed to enhance electrical conductivity of GO in the composite. The effect of electrochemical reduction is analyzed by detailed structural analysis. The relationship between the structure and electrochemical properties is examined by evaluating the performance of composites as EC electrodes. Preparation of the electrodes includes simple drop-casting method, which

provides direct observation of the effect of metal addition on the electrochemical performance of GO and rGO.

1.3.2. Layer-by-Layer Assembly of Metal (Hydr)oxide/Graphene Oxide

Thin Films as Electrodes for Electrochemical Capacitors

In Chapter 3, metal hydr(oxide) and GO are deposited successively on conductive substrates in layer-by-layer (LBL) fashion which results in production of multilayered structures composed of alternating metal and GO layers. Section 3.1 summarizes LBL assembly of nickel hydroxide/GO multilayers and their use of EC electrodes. Section 3.2 discusses LBL assembly of superparamagnetic iron oxide nanoparticles (SPION) and GO thin films. The interaction between SPION and GO is analyzed by means of state-of-the-art electron paramagnetic spectroscopy. The competition between defective carbon centers and superparamagnetic metal states is illustrated in terms of electrochemical properties. For all the LBL assembled thin films, powerful chemical reduction with hydrazine vapor is performed to enhance electrical conductivity of GO in the multilayered films. The nature of the charge storage mechanism is investigated for design of high performance EC electrodes.

1.3.3. Graphene Aerogels

In Chapter 4, a fascinating class of materials, graphene aerogels (GAs), is introduced. GAs are composed of randomly stacked graphene layers with ultralow density. The structural properties, production methods, drying techniques, and electrochemical properties of GAs reported in the literature are summarized and efficient preparation methods are suggested. Structural properties of the produced GAs are investigated in detail and electrochemical performance as an EC electrode and an ORR electrocatalyst are introduced.

1.3.4. Graphene Aerogel Supported Nickel Nanoparticles as

Electrocatalysts for Oxygen Evolution Reaction

In Chapter 5, GAs decorated with highly dispersed nickel nanoparticles are synthesized via one-step hydrothermal method followed by thermal reduction under H_2/He environment. Nickel loading is varied with changing Ni to GO ratio in the precursor solution. The effect of nickel loading on the electrocatalytic performance towards OER is investigated in detail with hydrodynamic measurements.

1.3.5. Graphene Aerogel Supported Platinum Nanoparticles as

Electrocatalysts for Oxygen Reduction Reaction

In Chapter 6, GAs are deposited with Pt precursor via supercritical CO_2 assisted deposition. Following adsorption of Pt precursor, Pt nanoparticles are formed with thermal conversion. By simply tuning the conversion temperature, Pt nanoparticle size and reduction degree of GA are varied. The resulting ORR activity of Pt electrocatalysts are correlated with Pt particle size, surface chemistry, and surface area of the composites.

Chapter 2: Electrochemical Properties of Transition Metal/Graphene Oxide Composites

2.1. Introduction

Composites of graphene with transition metal or metal hydr(oxide) have attracted great interest due to combination of fascinating electrochemical properties of each material class. Graphene exhibit well-known extraordinary properties such as excellent electrical conductivity, high specific surface area, and mechanical strength. [71] On the other hand, transition metal and metal (hydr)oxides have been used in electrochemical energy storage devices for decades due to their stability in multiple oxidation state resulting in facile redox ability. [72] For the construction of graphene/metal composites, perfect graphene obtained via mechanical exfoliation is not desirable since it lacks surface functionalities or defects. [13] In this regard, graphene obtained from reduction of oxidized graphite, reduced graphene oxide (rGO), has been widely utilized. The precursor of rGO, graphene oxide (GO), has abundant oxygen functional groups and defects that can serve as anchoring sites for metals. [73,74] Furthermore, the oxygen functional groups and defects can undergo redox reactions and exhibit pseudocapacitive properties. [46,75]

There are several methods to produce graphene/metal composites, classified into *ex situ* and *in situ*; *ex situ* methods include reaction of graphene derivatives with pre-synthesized metal (oxide) nanostructures whereas *in situ* methods consist of crystallization of the metal while reducing GO. [76] Numerous studies have been undertaken *in situ* techniques, such as microwave-assisted synthesis [77], chemical reduction [78], electrodeposition [79], hydrothermal [80], electroless deposition [81], and chemical bath deposition [82]. Although there are a vast number of studies regarding graphene/metal (oxide) composites, comparison of different metals on the electrochemical performance of GO and rGO needs further investigation for designing new composites. For that purpose, the synthesis method should be as simple as possible to understand the fundamental characteristics of the composites without the interference of foreign compounds,

such as reducing agents or crosslinkers. One of the facile methods for the production of graphene/metal composites was reported by Matsumoto et al. [83]. In this report, metal oxide/rGO composites were synthesized by photoelectrochemical reduction of GO electrodes from divalent metal cation containing solutions (Ni^{2+} , Co^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Ce^{3+}). Produced electrodes had areal capacitances around 20 mF cm^{-2} , the highest being the CoO_x/rGO one.

This chapter includes synthesis of first-row transition metal/GO composites via simple electrostatic precipitation technique. Negatively charged GO layers were simply mixed and sonicated with positively charged divalent transition metal cations (Co^{2+} , Ni^{2+} , Mn^{2+} , Fe^{2+}). Produced solutions were utilized to investigate the structural and electrochemical properties of the composites. Quantitative determination of the metal content bound to GO layers were conducted by ICP-MS analysis. Surface morphology and chemistry were investigated by FESEM, XPS, ATR-IR, and Raman measurements. Effect of electrochemical reduction on the electrochemical properties of the composites were evaluated by CV measurements. Electrochemically reduced composites' electrocatalytic activities towards ORR were determined with RDE setup.

2.2. Materials & Methods

2.2.1. Materials

All the chemicals were used as received without further purification. Graphite (natural, -200 mesh, 99.9995%), Na_2SO_4 (99%), KOH (ACS reagent grade), K_2SO_4 (99%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98.0%), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (99%), and NaNO_3 (99%) were purchased from Alfa Aesar. KMnO_4 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>99.0) and H_2O_2 (30%) were obtained from Merck Millipore. HCl (37%), H_2SO_4 (95-97%), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (>99.0%), and Nafion[®] perfluorinated solution (5 wt% in lower aliphatic alcohols and water) were obtained from Sigma Aldrich. Saturated calomel electrode (SCE, in saturated KCl) was purchased from Radiometer Analytical SAS, France. Reversible hydrogen electrode (RHE) was obtained from Gaskatel GmbH, Germany.

2.2.2. Synthesis of Graphene Oxide

Graphite oxide was synthesized from graphite by a modified Hummers method. [9] First, NaNO_3 (2 g) and graphite (2 g) were dissolved in ice cold concentrated H_2SO_4 solution. KMnO_4 (12 g) was added slowly to the mixture keeping the temperature below 5 °C by immersion of the reaction vessel in an ice bath. Afterwards, the temperature of the solution was slowly raised by addition of distilled water. Then, the mixture was heated to 75 °C and maintained at this temperature for 30 minutes. The reaction was terminated by the addition of 200 mL of distilled water and 10% H_2O_2 until the yellow foam disappeared. The resulting powder was washed twice with 5 wt.% HCl followed by distilled water. To obtain the exfoliation solution, approximately 0.3 g of graphite oxide powder was added to 100 mL of distilled water and placed into an ultrasonic bath for at least 4 hours. For the elimination of aggregated nanosheets, solutions were centrifuged at 10,000 rpm for 30 minutes and the supernatant solutions were stored. The exfoliation solution of graphene oxide (GO) nanosheets is called GO solution.

2.2.3. Synthesis of Transition Metal/GO composites

0.1 M of metal salt solutions (Co^{2+} , Ni^{2+} , Mn^{2+} , and Fe^{2+}) and GO solution (GO:metal ratio approximately 1:1 by mass) were stirred for 30 min and sonicated for further 1 h to ensure complete mix. Final GO concentration was 1.875 mg mL^{-1} . Resulting composites were named thereafter metal/GO (where metal is the element symbol for the corresponding metal cation).

2.2.4. Electrochemical Reduction of Transition Metal/GO Composites

5 μL of metal/GO solution was drop-casted onto freshly cleaned and polished HOPG substrate (diameter: 3mm, active area: 0.0707 cm^2) and dried at 60 °C for 1 h in air. For the electrochemical reduction, 3-electrode electrochemical setup was used, which was controlled with a potentiostat (Biologic VSP). HOPG loaded with metal/GO, Pt sheet, and SCE (sat'd KCl) was used as working, counter, and reference electrode, respectively. -1.145 V (vs SCE) was applied for 30 min in 0.1 M Na_2SO_4 solution. After the reduction, the electrode is rinsed with distilled water and left

to dry at RT. Reduced samples were named as rmetal/GO (where metal is the element symbol for the corresponding metal cation).

2.2.5. Structural Characterization of Produced GO

Crystal structure of GO was investigated with X-ray diffraction (XRD, Bruker D8 Advance) with Cu K α source. For XRD, 5 mL GO solution was filtered through cellulose nitrate paper (pore size: 0.45 μ m, Sartorius AG). Self-standing GO paper was peeled off from the filter paper after air drying. Approximately 1 cm x 1 cm piece of GO paper was used for XRD measurement. Analysis of defects in GO was conducted with Raman (Renishaw Invia) with 532 nm laser. Atomic force microscopy (AFM) images of GO were collected with Bruker Dimension Icon in ScanAsyst mode (tapping). For AFM, 1 drop of 1:400 diluted 5 mg mL⁻¹ GO solution was dried onto freshly cleaved mica sheet piece. Surface chemical structure of GO was analyzed with X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha) with Al K α source.

2.2.6. Structural Characterization of Transition Metal/GO Composites

For facile characterization of the composites, 70 μ L of metal/GO was drop-casted onto ITO substrates (1 cm²) and dried at 60 °C for 1 h. For more accurate representation of the samples, Co/GO and Ni/GO thin films were immersed in 1 M KOH solution (which is the CV electrolyte) for 1 min, followed by immersion in distilled water and air drying. Mn/GO and Fe/GO thin films were only immersed in distilled water for 1 min to eliminate physically adsorbed metal cations and counter anions. For the reduced versions of composites, same electrochemical reduction route introduced in Section 2.2.4. was applied to ITO electrodes coated with metal/GO.

Morphology of the deposited films were investigated with Field Emission Scanning Electron Microscopy (FESEM, Zeiss Ultra Plus). For the crystal structure analysis of metal oxides and defect analysis of GO, Raman spectroscopy (Renishaw Invia) was utilized. The laser power was adjusted to 0.1 mW to avoid local heating and phase transformation via oxidation of metal cations. The fittings for the experimental data were done with Fityk software. Surface chemical structure of the films were analyzed with XPS (Thermo K-Alpha) with Al K α source. The fittings for the

experimental data were done with Advantage software. To determine the metal amount on the GO sheets, inductively coupled plasma mass spectroscopy (ICP-MS, Agilent 7700x) was utilized. Briefly, metal/GO solutions were centrifuged at 10000 rpm for 10 min, and the supernatant solution was subjected to ICP-MS measurement along with the reference metal salt solutions with known concentrations (not mixed with GO). Back-calculation gives the amount of metal amount precipitated (bound) on GO according to the following equation:

$$\text{metal precipitated (\%)} = \frac{(m_{ref} - m_{supernatant})}{m_{total}} \times 100 \quad (2-1)$$

where m_{ref} represents mass of metal in the reference solution, $m_{supernatant}$ represents mass of metal remained after centrifuge, and m_{total} is the total mass of metal and GO initially.

2.2.7. Electrochemical Characterization of Transition Metal/GO Composites

Electrochemical properties of metal/GO were investigated primarily with cyclic voltammetry (CV) measurements via 3-electrode electrochemical setup connected to the potentiostat. The working electrodes were prepared by drop-casting 5 μL of metal/GO solutions onto HOPG electrodes followed by drying at 60 $^{\circ}\text{C}$ for 1h. Then, 5 μL of 0.2 mg mL^{-1} nafion solution was dropped onto the dried film for stabilizing films followed by further drying at 60 $^{\circ}\text{C}$ for 1 h. For Co/GO and Ni/GO, HOPG electrode loaded with composite, Pt sheet, and RHE was used as working, counter, and reference electrode, respectively. The electrolyte was 1 M KOH. For Mn/GO and Fe/GO, reference electrode was SCE (sat'd KCl) and the electrolyte was 0.5 M K_2SO_4 . For each composite and the reduced counterparts, the electrodes were scanned with scan rates ranging from 100 to 5 mV s^{-1} . Cyclic stability tests were conducted at 100 mV s^{-1} for 3000 cycles in the corresponding metal working potential range. For rotating disk electrode (RDE) measurements, home-made glassware electrochemical cell setup was used. The working electrode was RDE (OrigaTrod, OrigaTrod kit) coupled with metal/GO loaded glassy carbon tip (diameter: 3mm, active area: 0.0707 cm^2), counter electrode was Pt sheet, and the reference electrode was RHE. Electrolyte solution for all RDE measurements was 0.1 M KOH for all metals. Prior to measurements,

electrolyte was saturated with N_2 gas for at least 20 min to obtain CV curves in absence of O_2 . Then, the electrodes were scanned between 0.0-1.3 V vs RHE at 50 mV s^{-1} for 20 cycles. Following this measurement, bubbling gas is switched to O_2 for further 20 min. After reaching saturation, ORR polarization curves were obtained in the potential range 0.0-1.0 V vs RHE at 5 mV s^{-1} .

2.3. Results & Discussion

2.3.1. Structural Properties of Produced Graphene Oxide

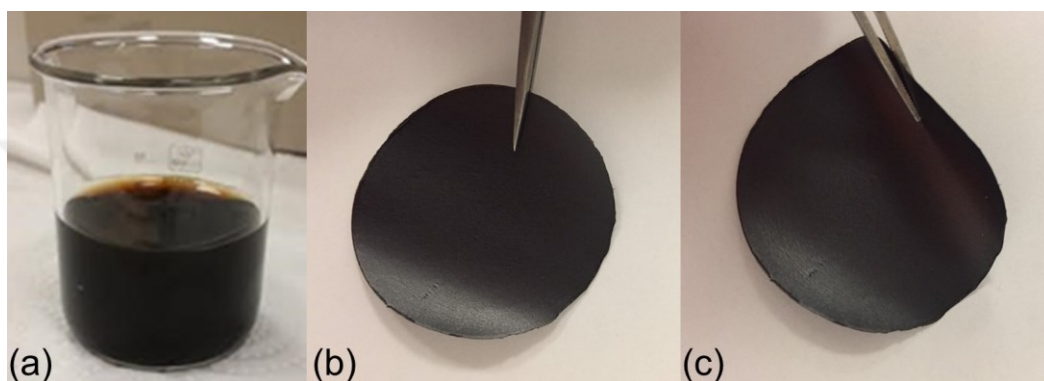


Figure 2-1 Digital image of (a) GO solution (b,c) self-standing GO paper

Following the experimental procedure in Section 2.2.2. , brown exfoliation solution was obtained as shown in Figure 2-1. For the determination of concentration, 5 mL GO solution was filtered through a cellulosic filter paper and air-dried. GO paper was peeled off from the filter paper, and the mass was recorded. By dividing this mass to the volume of initial solution, concentration in mg mL^{-1} was calculated. This procedure was repeated for at least 3 times until a consistent value was obtained. The digital image of self-standing GO paper can be seen in Figure 2-1.

For the confirmation of the production of single nanosheets, AFM was utilized. Figure 2-2 shows AFM images of GO synthesized via modified Hummers method. Height profiles reveal that all nanosheets have average thickness of 1.1 nm, indicating the nanosheets contain oxygen functional groups. [16] Nanosheets with lateral sizes as large as $8.0 \mu\text{m}$ (Figure 2-2c) are observed along with

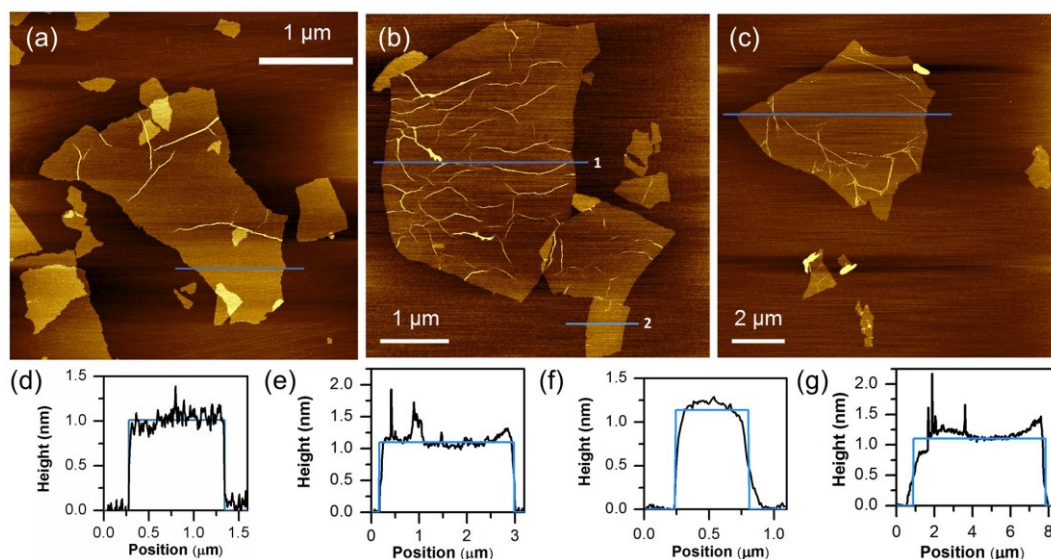


Figure 2-2 AFM images and corresponding height profiles of GO nanosheets. (d) is the height profile for the line in (a), (e,f) are the height profiles of line 1 and 2 in (b), respectively, (g) is the height profile for the line in (c)

several smaller ones. Thus, single GO nanosheet solution was successfully synthesized by the modified Hummers method.

The crystal structure of GO was further analyzed by XRD and Raman. Figure 2-3a shows the XRD diagram of GO paper. The diagram has one sharp peak at $2\theta=10.95^\circ$ which corresponds to an interlayer spacing of 0.81 nm. This value is much higher than that of precursor graphite, which is 0.337 nm indicating a drastic increase in the interlayers due to presence of oxygen functional groups. [84] Raman spectrum of GO consists of two dominant peaks around 1350 and 1585 cm^{-1} corresponding to D and G band of diamond and graphite, respectively (Figure 2-3b). [85] While it has been claimed that the intensity ratio of these two bands (I_D/I_G) gives sufficient information about the quantity of defects in the structure; in recent studies, researchers utilize a deconvolution process for a more accurate defect analysis. [86] Accordingly, two broad peaks are deconvoluted into five peaks, using two Gaussian and three Pseudo-Voigt peaks (Figure 2-3b). The first peak around 1100 cm^{-1} , D* (Gaussian), is related with the disordered graphitic lattice. The second one is D band (pseudo-Voigt) around 1350 cm^{-1} , defect-induced Raman mode of graphite which is not observed in perfect graphitic structures.[87] D'' band (Gaussian) around 1500 cm^{-1} is related with

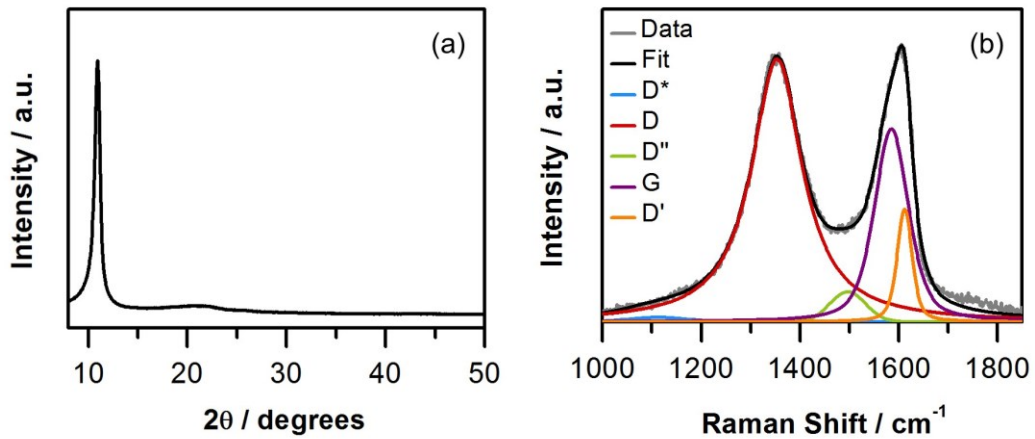


Figure 2-3 (a) XRD diagram of GO paper (b) Fitted Raman spectrum of GO

the presence of amorphous phases. While G band (pseudo-Voigt) around 1580 cm^{-1} belongs to defect-free graphite, D' (pseudo-Voigt) at 1610 cm^{-1} is the disorder-induced phonon mode due to crystal defects. [86] In this regard, all the aforementioned bands give valuable information about the crystal structure of produced graphene derivative. Table 2-1 shows the corresponding peak ratios calculated from deconvolution of Figure 2-3b.

Table 2-1 Fitting results of GO Raman spectrum

I_{D^*}/I_G	I_D/I_G	$I_{D''}/I_G$	$I_{D'}/I_G$
0.02	1.36	0.16	0.59

Identification of oxygen functional groups of GO was conducted with ATR-IR spectroscopy. In the IR spectrum of GO (Figure 2-4), a broad peak centered around 3200 cm^{-1} is a result of free water intercalated in between layers of GO and the structural hydroxyl groups (COOH and COH). [88] Additionally, the peak at 1720 cm^{-1} is assigned to C=O stretching of carboxyl groups, 1625 cm^{-1} is the bending mode of water hydrating the carboxylic group, 1420 , 1200 and 1040 cm^{-1} are C-O stretching of carboxyl, hydroxyl, and epoxide groups, respectively.[88–91] The presence of the vibrational modes of these carbon-oxygen functional groups verifies the oxidation of graphite, in agreement with AFM and XRD results.

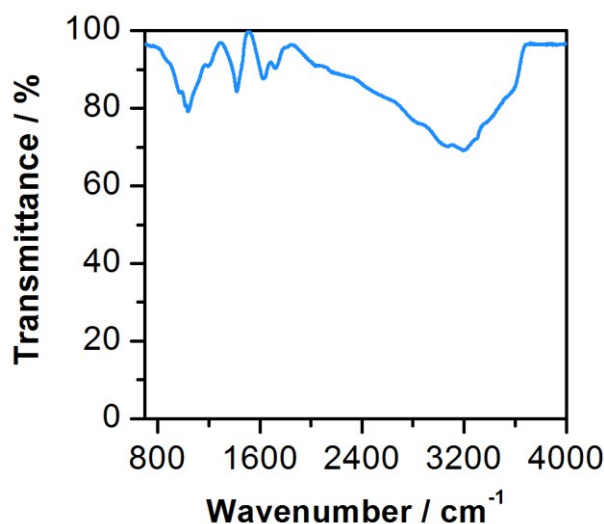


Figure 2-4 ATR-IR spectrum of GO

XPS is a powerful tool for the evaluation of oxygen functional groups produced on GO both qualitatively, and quantitatively. XPS C1s spectrum of GO (Figure 2-5a) is deconvoluted into three peaks, which belong to carbon-carbon (C-C/C=C/C-H), carbon-oxygen (hydroxyl and epoxy), carbon=carbon (carbonyl and carboxyl) bonds at 284.5, 286.5, and 288.0 eV, respectively. [16] Relative intensities of the functional groups normalized to C-C are directly related to the amounts of these individual groups present on the structure. From Figure 2-5a, I_{C-O}/I_{C-C} and $I_{C=O}/I_{C-C}$ are calculated as 1.25 and 0.15, respectively. O 1s spectrum of GO is deconvoluted into three peaks: O doubly bonded to aromatic C, O singly bonded to aliphatic C, and O singly bonded to aromatic

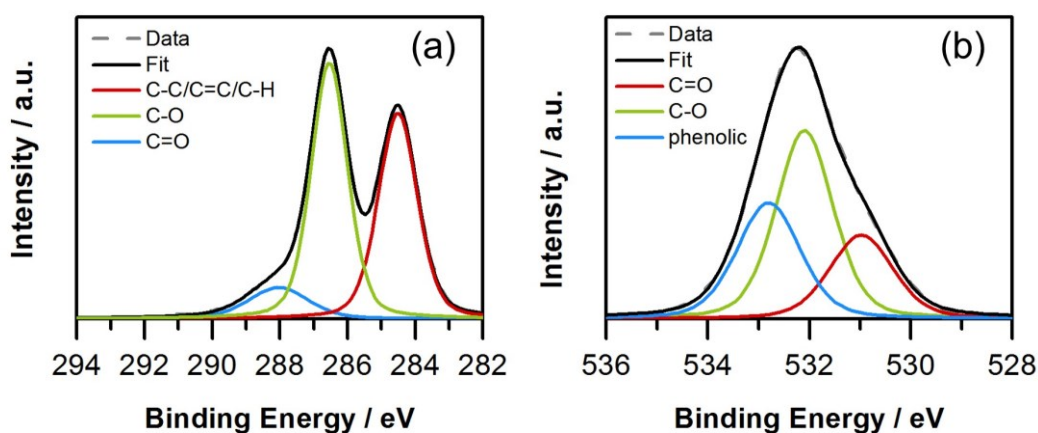


Figure 2-5 XPS (a) C1s (b) O1s spectrum of GO

C (phenolic) at 531.0, 532.1, and 532.8 eV, respectively (Figure 2-5b). [84] Consistent with the C1s spectrum, C=O has the least contribution to the overall peak area in O1s spectrum.

2.3.2. Structural Properties of Transition Metal/GO Composites

Mixing GO and metal salt solutions result in instant formation of gel-like solutions, but quite stable for weeks. ICP-MS measurements were conducted to analyze the amount of ions precipitated with GO from a known concentration of salt solution (0.025 M). Corresponding values are given in Table 2-2. The results showed good linearity as indicated by the high R^2 values for calibration curves.

Table 2-2 ICP-MS results of GO/metal solutions

Sample	Metal bound to GO (%)	R^2 values
Co/GO	8.67	0.9999
Ni/GO	1.27	0.9999
Mn/GO	4.81	0.9999
Fe/GO	31.4	0.9998

As seen from the percentages given in Table 2-2, each metal cation interacts differently with GO layers. All these metal cations forms hexaaqua complexes in aqueous solutions as represented in Figure 2-6. The four metal cations used in this study are all first-row transition metals and according to *crystal field theory*, degenerate 3d orbitals of these metals are split into two different energy levels (t_{2g} and e_g) due to asymmetric pointing of d orbitals. The energy difference between the split orbitals (Δ_{oct}) for an octahedral crystal is determined by the strength of the ligand attached to the metal ion. The arrangement of electrons in the split d levels is also dependent on the strength of ligands: strong field ligands favor low-spin configuration, and weak field ligands favor high-spin configurations. [92] Since water is a weak field ligand, all the considered metal cations here forms

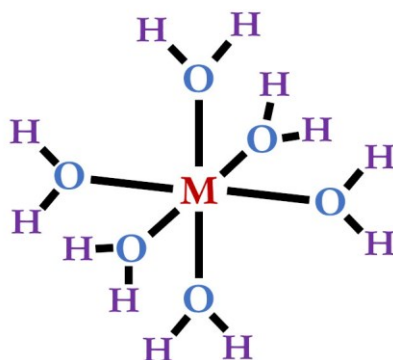


Figure 2-6 Chemical structure of $[M(OH_2)_6]^{2+}$ complex

high-spin octahedral complexes with water as shown in Figure 2-7. [93] Normally, one would expect that the oxygen functional groups would easily replace the water molecules since these functional groups are stronger field ligands than water in the spectrochemical series. [92] However, previously discussed results showed that the presence of water molecules around transition metal center causes a substantial reduction in the binding energies (around 100-160 kcal mol⁻¹) due to orbital unavailability of metal center. [94] Consequently, it has been stated that the interaction between hydrated metal centers and outer ligands is purely electrostatic. [94,95] For the first-row transition metals in high-spin octahedral crystal field, the electronegativity values increase steadily from Mn to Ni (Mn: 1.263, Fe: 1.292, Co: 1.321, Ni: 1.367). [96] This trend suggests that the electrostatic interaction between metal and negatively charged ligands should be in the following order: Mn > Fe > Co > Ni. However, Table 2-2 indicated that the metal-GO affinity follows the trend Fe > Co > Mn > Ni, suggesting that Mn is bucking the trend. The affinity of a metal towards a ligand can be also rationalized with the well-known *Pearson hard and soft acids and bases principle* (HSAB). [92] According to HSAB, all ligands (Lewis bases) and metal centers (Lewis acids) are classified as hard, soft, or intermediate depending on their polarizability. Hard acids tend to form stable compounds with hard bases, and soft acids favor soft bases. The stability of the resulting

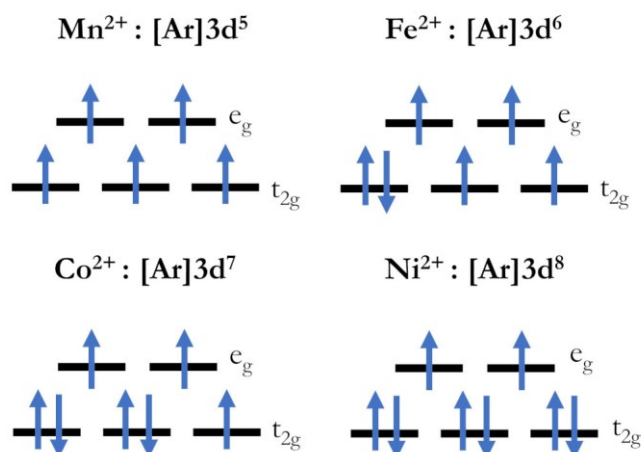


Figure 2-7 Electron configurations and arrangements of Mn^{2+} , Fe^{2+} , Co^{2+} , and Ni^{2+} in the high-spin octahedral crystal field

complex is dependent on the hard-hard (or soft-soft) interactions between the metal cations and ligands. In this regard, Mn^{2+} is the only hard acid among the studied metal cations (others are classified as intermediate) which have strong hard-hard interaction with water molecules. Thus, ligand substitution is not favorable for Mn^{2+} resulting in lower metal-GO interaction.

ATR-IR spectra of metal/GO in comparison with that of GO are given in Figure 2-8. The pronounced C=O stretching observed in GO spectrum (1720 cm^{-1}) is not distinguishable in any of the metal/GO spectrum. Both O-H and C-O stretching peaks of carboxyl groups (1620 and 1420 cm^{-1}) broadened and red-shifted in metal/GO spectra compared to that of GO suggesting that there is a particular interaction of these species with the metal center. Interestingly, C-O stretching peak of hydroxyl groups (1200 cm^{-1}) seems to be vanished upon addition of metal to GO. C-O stretching peak of epoxy groups (1040 cm^{-1}), however, either blue-shifted in metal/GO spectra compared to GO, or the original peak position in GO was not identified accurately due to overlapping of several peaks. The strong absorbance of Fe/GO below 1000 cm^{-1} is probably due to interference of Fe-O stretching vibrations around $400\text{-}600 \text{ cm}^{-1}$ since this composite has the highest amount of metal ion. [97] Nevertheless, the shift and the decrease in intensities of the

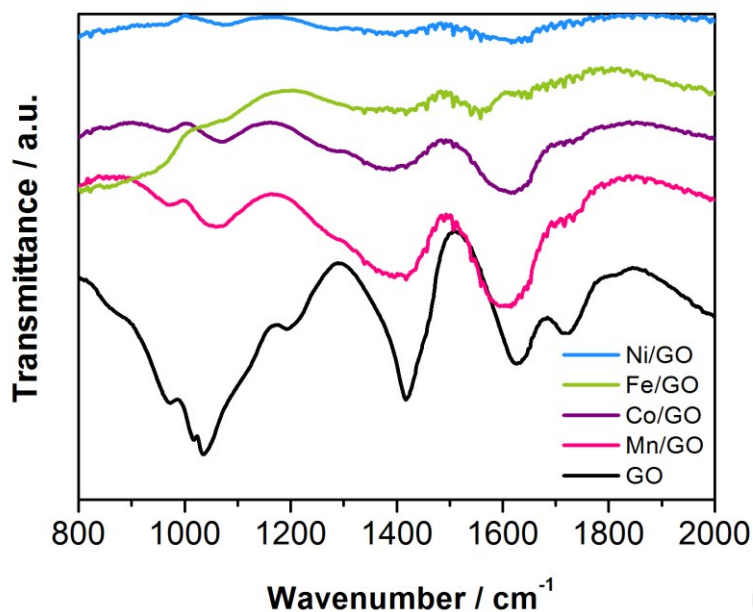


Figure 2-8 ATR-IR spectra of GO and metal/GO

peaks indicate that there is a strong interaction between C-OH end of carboxyl groups and hydroxyl groups with the metal ions. [98–100]

Raman spectroscopy is utilized to investigate the crystalline structure of metal/GO composites. In the Raman spectra of all metal/GO composites (Figure 2-9a), D and G bands are observed that are explained in detail in Section 2.3.1. To investigate the defects and the crystalline structure more exclusively, the peaks under D and G bands are deconvoluted into five peaks as in Section 2.3.1. The corresponding fitting results along with that of reduced samples (Figure 2-9b) are tabulated in Table 2-3. Enlarged fitted D and G band regions are given in Figure 2-10. After electrochemical reduction, I_D/I_G ratio increased in all metal/GO indicating increase in defects during the reduction process. Conversely, decrease is observed in I_{D^*}/I_G which is a result of deoxygenation of GO layers since I_{D^*}/I_G is related with the disordered graphitic lattice. Lastly, decrease in I_{D^*}/I_G after reduction indicates enhancement of crystallinity. [86] No peaks are observed in the 200-1000 cm^{-1} region in the metal/GO or reduced metal/GO Raman spectra (Figure 2-9). Thus, any metal oxide/hydroxide peaks are not visible.

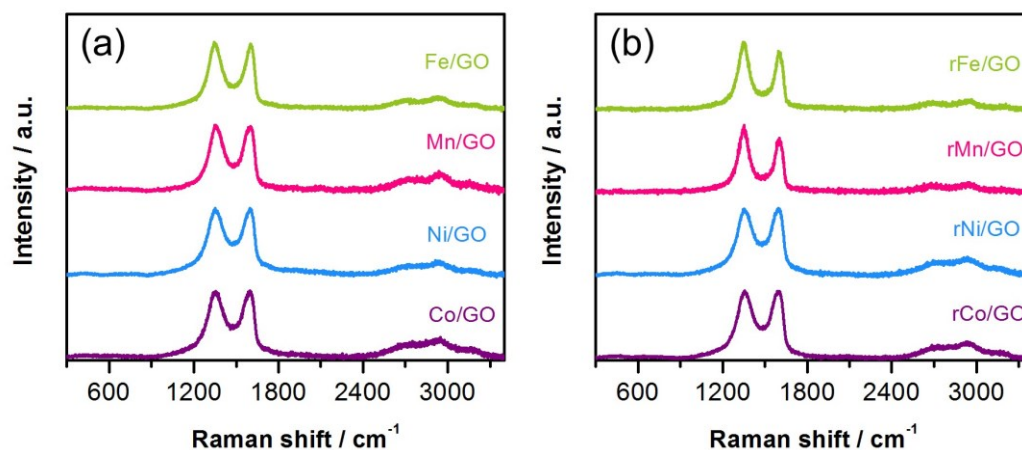


Figure 2-9 Raman spectra of (a) metal/GO (b) electrochemically reduced metal/GO

Table 2-3 Fitting results of Raman spectra of metal/GO and reduced metal/GO

Sample	I_D/I_G	I_{D^*}/I_G	$I_{D''}/I_G$
Co/GO	1.13	0.08	0.27
rCo/GO	1.14	0.03	0.20
Ni/GO	1.17	0.06	0.27
rNi/GO	1.59	0.03	0.26
Mn/GO	1.33	0.07	0.35
rMn/GO	1.55	0.04	0.23
Fe/GO	1.67	0.07	0.32
rFe/GO	1.48	0.03	0.23

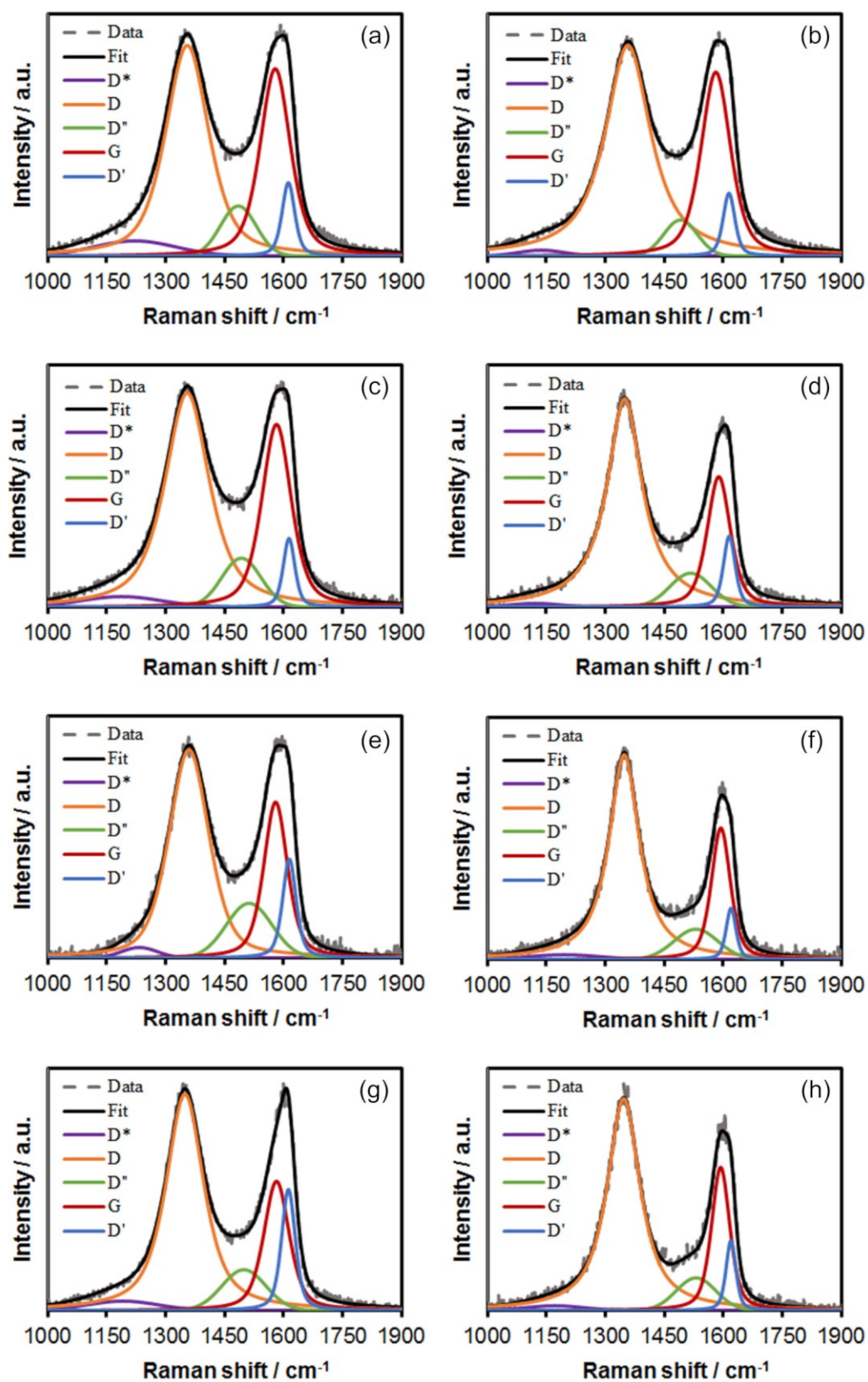


Figure 2-10 Fitted Raman spectrum of (a) Co/GO (b) rCo/GO (c) Ni/GO (d) rNi/GO (e) Mn/GO (f) rMn/GO (g) Fe/GO (h) rFe/GO

XPS C1s spectra of metal/GO are given in Figure 2-11. All the spectra resemble that of bare GO, consisting of three peaks of C-C, C-O, and C=O. Compared to bare GO, there is a significant decrease in the relative intensity of C-O in all metal/GO, except in that of Mn/GO (Table 2-4). The relative intensity of C=O, however, did not change significantly. The decrease in C-O peak may suggest that the metal cations are binding to these sites, rather than C=O. After electrochemical reduction, C-O peak intensity decreased drastically in all the rMetal/GO (Table 2-4), and C=O peak intensity decreased slightly, except in that of rFe/GO. XPS metal 2p spectra of metal/GO are given in Figure 2-12. Co 2p spectrum of Co/GO has $2p_{3/2}$ peak at 780.4 eV with a broad shoulder at 785.8 eV. The binding energy of principal peak and the satellite at 6 eV above the main peak belongs is typically observed in Co(II) bound to oxygen. [101] Although there is 1 eV energy difference and strong resemblance of spectral features between Co2p spectra of CoO and Co(OH)₂, the spectrum in Figure 2-12a matches with that of Co(OH)₂. [102] Ni 2p spectrum of Ni/GO shows $2p_{3/2}$ peak at 856.2 eV accompanied with a satellite at 861.9 eV (Figure 2-12b). The binding energy value and the spectral shape revealed that the Ni is in the form of Ni(OH)₂ in Ni/GO. [102] The metal hydroxide formation in both Co/GO and Ni/GO is reasonable since the thin films were washed with KOH in the sample preparation procedure as explained in Section 2.2.6. In Mn2p spectrum of Mn/GO, a broad $2p_{3/2}$ peak at 642.0 eV is observed with a broad shoulder around 647.1 eV (Figure 2-12c). The $2p_{3/2}$ is broader than that of Co/GO and Ni/GO due to multiple splitting of Mn 2p spectra. Nevertheless, the binding energy and the spectral features indicated that Mn is in 2+ oxidation state as in MnO. [103] Lastly, Fe 2p spectrum of Fe/GO (Figure 2-12d) exhibited a broad $2p_{3/2}$ peak around 710.8 eV with no pronounced satellite. Determination of iron oxidation state from XPS is problematic due to the closeness of binding energies between 2+ and 3+ oxidation states and the extreme sensitivity of iron oxide surfaces when bombarded with high energy x-rays. Nevertheless, Fe in Fe/GO is identified in between 2+ and 3+ when comparing binding energies of individual oxidation states. [104,105] After electrochemical reduction, there is no significant change in the metal 2p spectra indicating that the

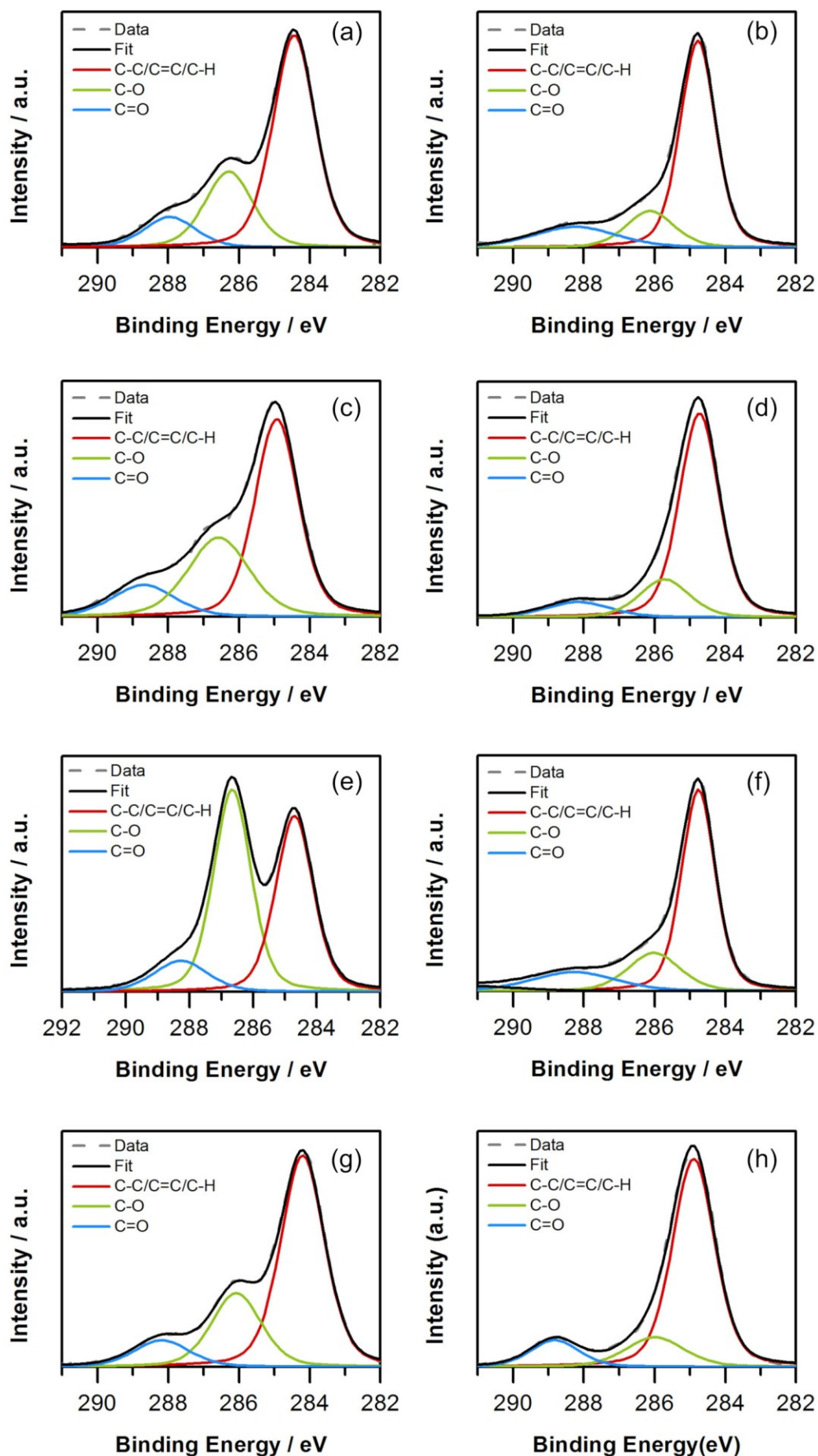


Figure 2-11 XPS C1s spectrum of (a) Co/GO (b) rCo/GO (c) Ni/GO (d) rNi/GO (e) Mn/GO (f) rMn/GO (g) Fe/GO (h) rFe/GO

oxidation states of metal centers remain unchanged during the reduction process of GO (Figure 2-12).

Table 2-4 Relative intensities of carbon-oxygen functional groups in GO/metal composites calculated from XPS C1s spectra

Metal	Metal/GO		rMetal/GO	
	C-O	C=O	C-O	C=O
Co	0.41	0.18	0.18	0.10
Ni	0.40	0.16	0.19	0.08
Mn	1.15	0.17	0.19	0.10
Fe	0.35	0.13	0.14	0.13

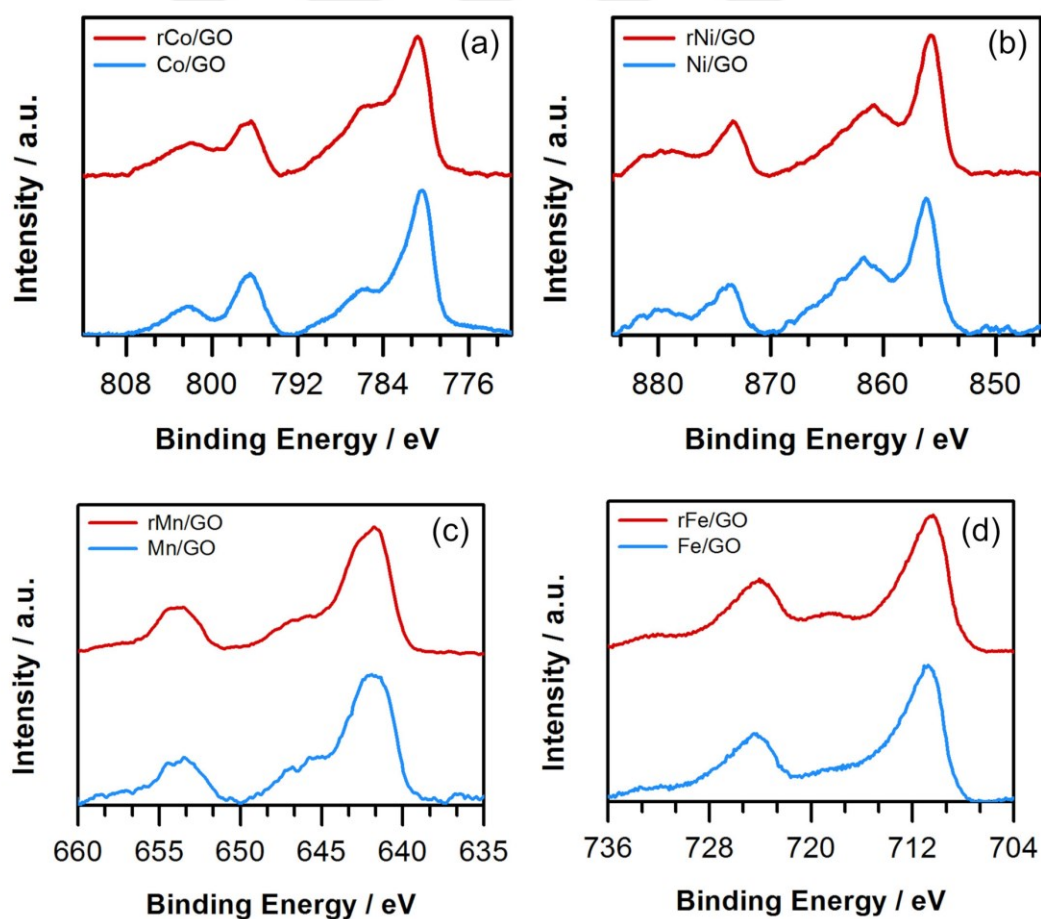


Figure 2-12 XPS (a) Co₂p (b) Ni₂p (c) Mn₂p (d) Fe₂p spectra of the corresponding GO/metal composites

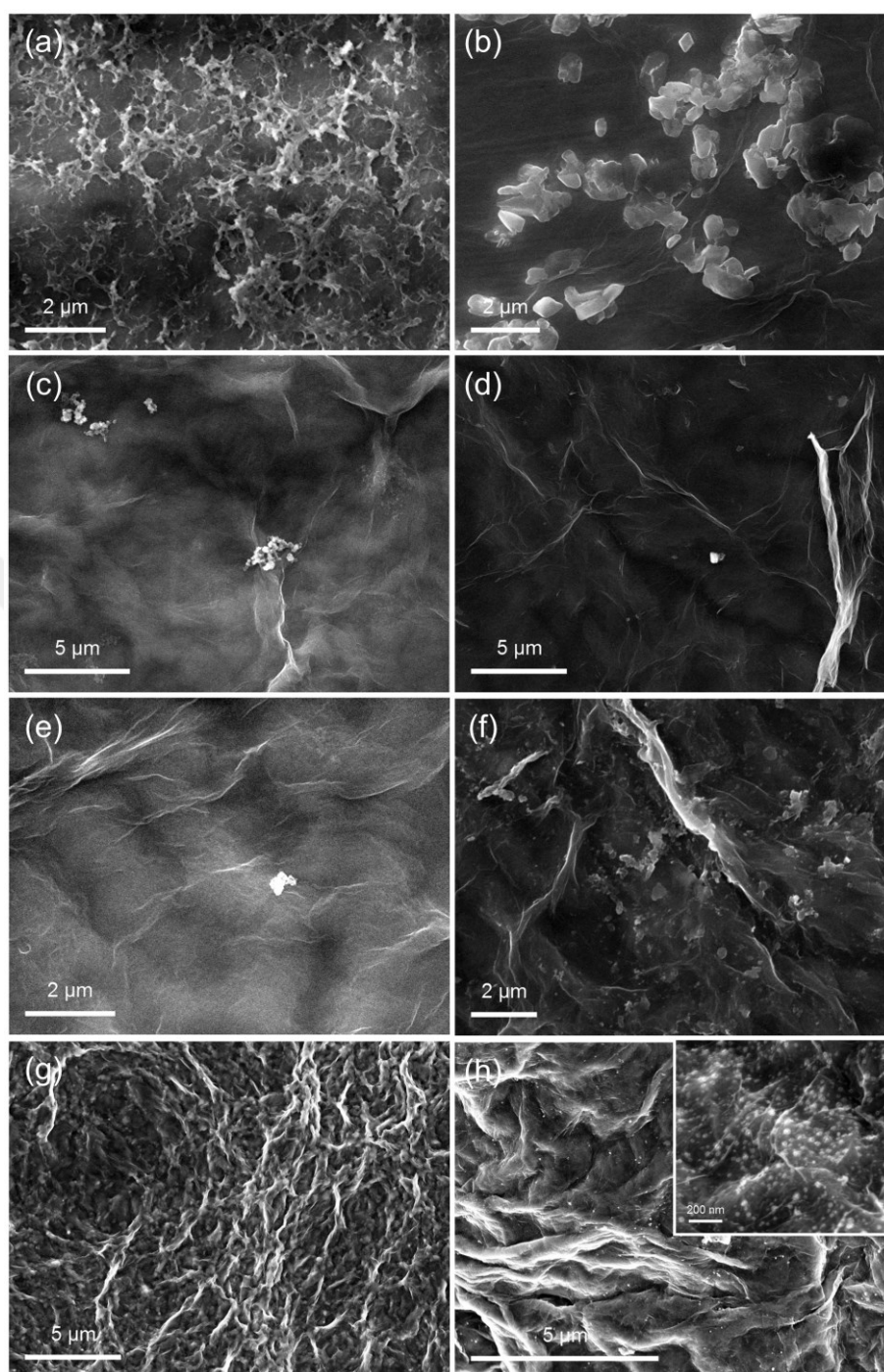


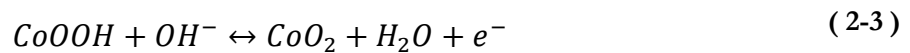
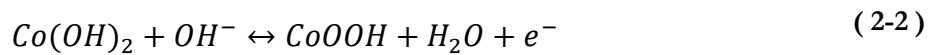
Figure 2-13 FESEM images of (a) Co/GO (b) rCo/GO (c) Ni/GO (d) rNi/GO (e) Mn/GO (f) rMn/GO (g) Fe/GO (h) rFe/GO inset shows higher magnification image of rFe/GO

FESEM images of all the metal/GO and reduced metal/GO are shown in Figure 2-13. FESEM image of Co/GO (Figure 2-13a) exhibits GO sheets decorated with aggregated particles which are probably $\text{Co}(\text{OH})_2$ as verified with XPS results. After reduction, aggregated small particles enlarged to form larger ones. In Ni/GO (Figure 2-13c), the concentration of particles distributed on GO

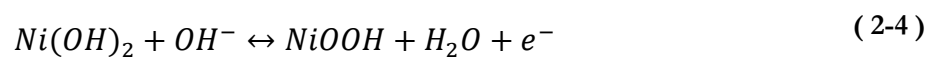
layers is much lower than that of Co/GO. There is no significant change in the morphology after reduction (Figure 2-13d). The structure looks similar to Ni/GO in Mn/GO (Figure 2-13e), although observed particles are increased in concentration after reduction (Figure 2-13f). Upon addition of iron to GO, the layered structure of GO changed drastically (Figure 2-13g). GO layers formed a 3D-like network with random stacking accompanied with highly dispersed iron (probably oxide) nanoparticles (Figure 2-13h). The morphology is almost unchanged during electrochemical reduction (Figure 2-13h). In fact, small iron oxide nanoparticles with approximate diameters of 20 nm are visible in higher magnification images.

2.3.3. Electrochemical Properties of Transition Metal/GO Composites

CV measurements were utilized to investigate the electrochemical properties of metal/GO composites. Figure 2-14 shows cyclic voltammograms of metal/GO composites and their reduced counterparts at scan rate of 20 mV s⁻¹. As validated with XPS results in Section 2.3.2, cobalt and nickel in Co/GO and Ni/GO are in the form of Co(OH)₂ and Ni(OH)₂, respectively. Consequently, cyclic voltammogram of Co/GO exhibits two pairs of peaks which result from the following redox reactions of cobalt hydroxide in alkaline medium (1 M KOH):



The peaks at lower potential side is the quasireversible process of equation (2-2), and the peaks at higher potential side signifies the reaction in equation (2-3). [106,107] In the cyclic voltammogram of Ni/GO, there are two peaks at 1.30 and 1.41 V (vs RHE) in cathodic and anodic side, respectively. The one at 1.41 V belongs to formation of nickel oxyhydroxide from nickel hydroxide in alkaline solution:



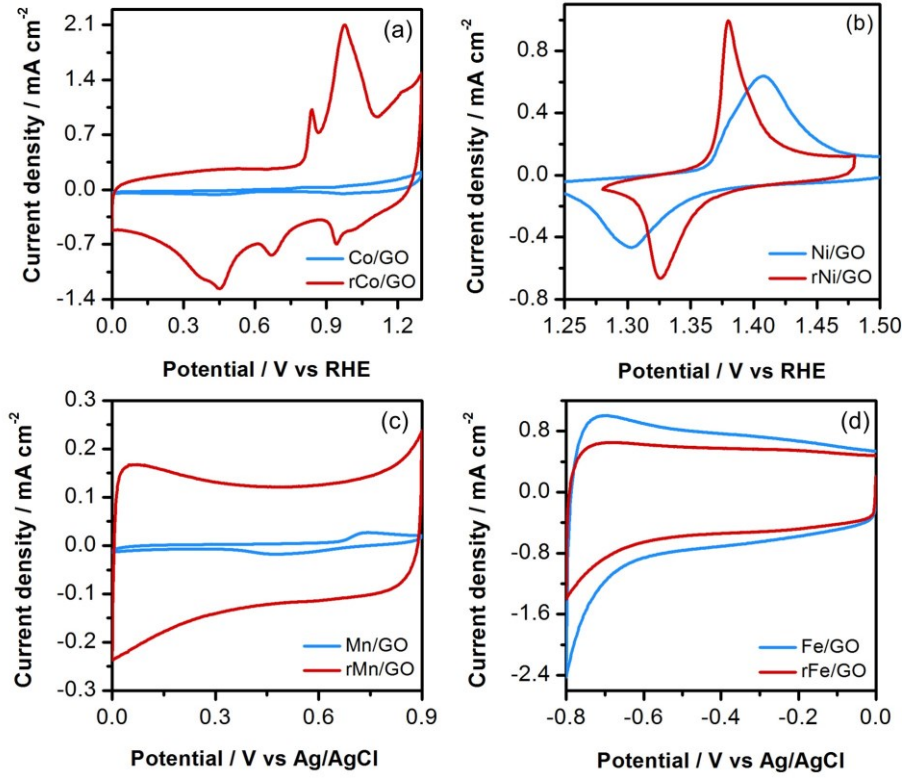
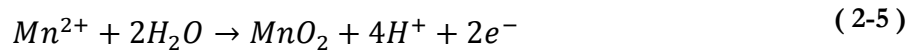


Figure 2-14 Cyclic voltammograms of GO/metal composites and their reduced counterparts. Scan rate: 20 mV s⁻¹

where the peak in the cathodic side is due to the reverse process. [108] CV curve of Mn/GO consists of two peaks at 0.74 and 0.48 V (vs Ag/AgCl) in anodic and cathodic side, respectively. These peaks are identified as the formation of MnO₂ from free Mn²⁺ cation according to the following equation [109]:



In CV curve of Fe/GO, no detectable redox peaks are observed since iron (oxides) does not exhibit any pronounced redox peaks in the potential range of interest in neutral electrolyte (0.0 – (-0.8) V (vs Ag/AgCl)). [110] In all the composites, the current densities and the area enclosed by the curves increased except in that of Fe/GO (Figure 2-14). The areal capacitance values of all metal/GO and reduced metal/GO are tabulated in Table 2-5.

Table 2-5 Electrochemical properties of metal/GO composites

Metal	Metal/GO	rMetal/GO	Ratio of areal	GO	rGO
	Areal capacitance	Areal capacitance	capacitances	contribution	contribution
	(mF cm ⁻²)	(mF cm ⁻²)	rMetal/GO: Metal/GO	%	%
Co	2.04	31.6	15.5	26.1	40.3
Ni	7.07	8.91	1.26	2.17	69.1
Mn	0.43	6.86	15.9	17.7	117.4
Fe	38.7	29.1	0.75	6.10	42.4

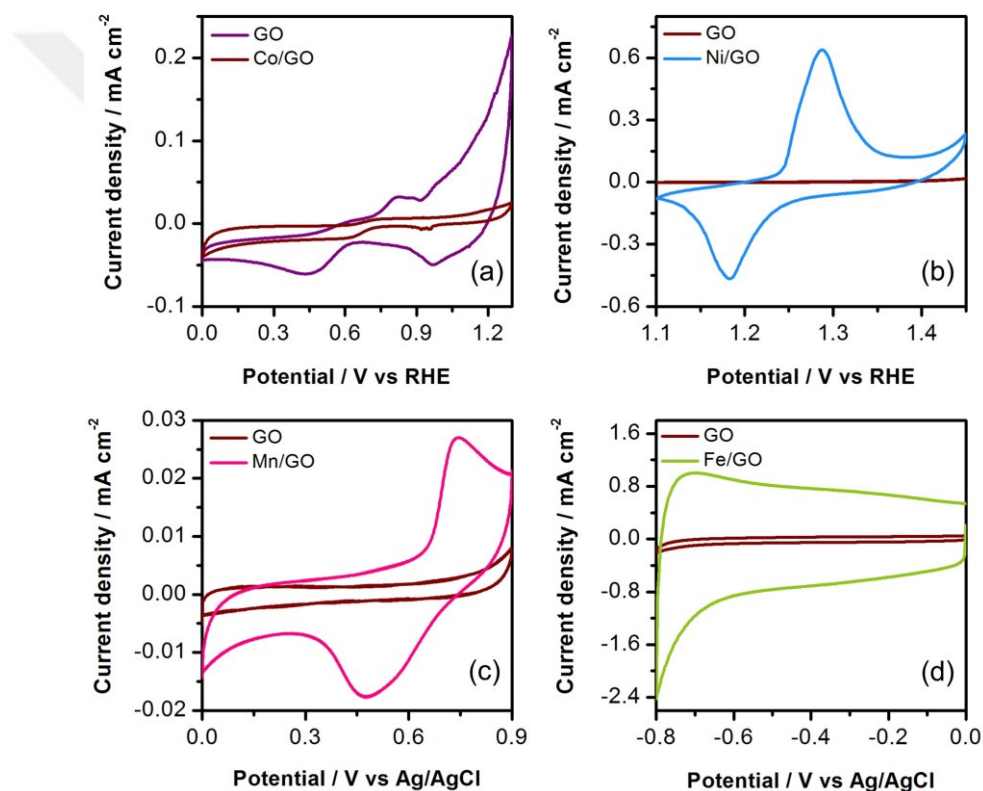


Figure 2-15 Cyclic voltammograms of GO and metal/GO composites. Scan rate: 20 mV s⁻¹. Electrolyte solutions (a,b) are 1 M KOH and (c,d) are 0.5 M K₂SO₄

In fact, reducing Fe/GO caused reduction in areal capacitance. The working potential range of Fe/GO is in the negative potentials vs Ag/AgCl, and electrochemical reduction of GO to rGO is also previously reported in neutral electrolyte. [111] Thus, what we are analyzing as “non-reduced” Fe/GO is actually a reduced composite with increase in cycle number. Electrochemical reduction

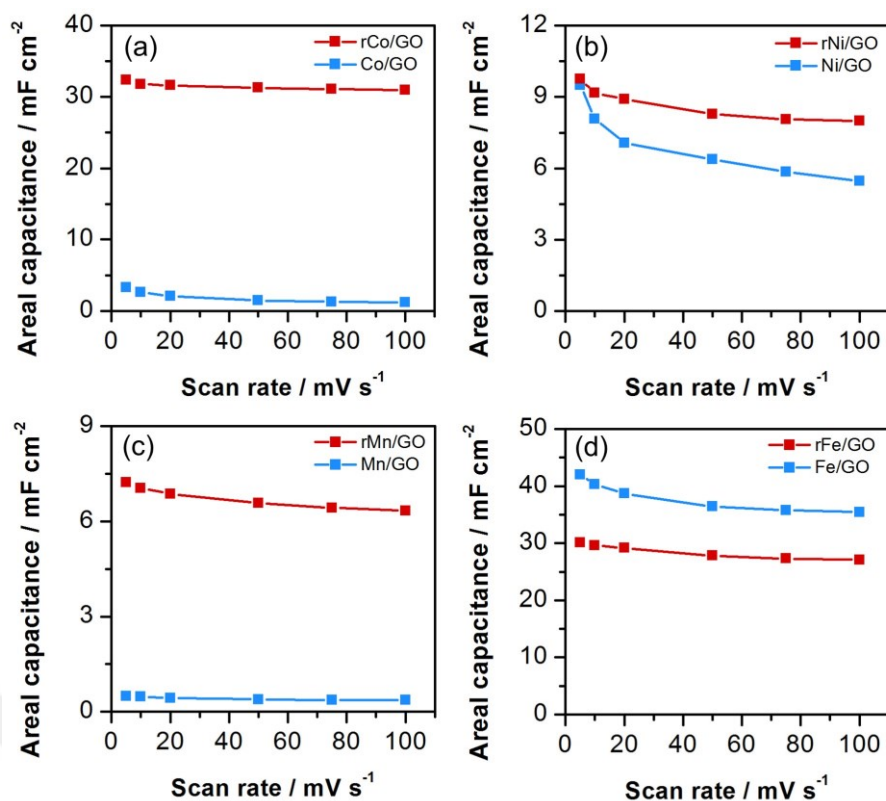


Figure 2-16 Areal capacitance change with scan rate for all metal/GO and their reduced counterparts

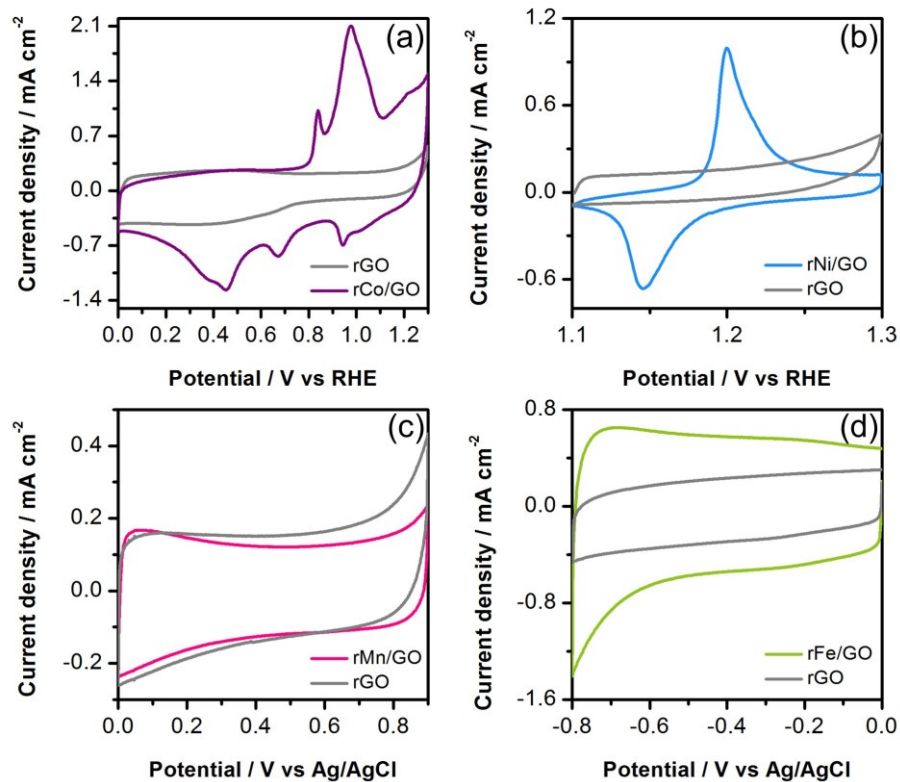


Figure 2-17 Cyclic voltammograms of rGO and rMetal/GO. Scan rate: 20 mV s⁻¹. Electrolyte solutions (a,b) are 1 M KOH and (c,d) are 0.5 M K₂SO₄

at -1.1 V for 30 min (which is more negative than the most negative potential in CV (-0.8V))

probably produced more reduced rGO with less functional groups. This caused a reduction in areal capacitance, since GO has higher capacitance than rGO due to pseudocapacitive effects arising from redox reactions of oxygen functional groups.[47] The change of areal capacitance values of metal/GO composites with scan rate is shown in Figure 2-16. Areal capacitance values decrease with increasing scan rate for all composites due to limited availability of redox-active centers and capacitive surfaces at faster charge-discharge rates. [36] Highest capacitance values at different scan rates are obtained with Fe/GO which has the highest metal amount according to ICP-MS results. Fe/GO is followed by rCo/GO which has the second highest metal amount. Furthermore, while the areal capacitance of Co/GO and Mn/GO increased almost 16-fold after reduction, Ni/GO increased 1.30-fold. The areal capacitances obtained in this study are almost 2-fold higher for rCo/GO and rFe/GO, but lower for rNi/GO and rMn/GO than previously reported composites by simultaneous electrodeposition from GO and metal cation containing solutions. [83] The contribution of GO capacitance to the overall capacitance is calculated by measuring CV of bare GO in neutral (K_2SO_4) and alkaline (KOH) electrolytes for different metals in the same working potential range of corresponding metal. Cyclic voltammograms of metal/GO overlapped with bare GO at the same scan rate are shown in Figure 2-15. In alkaline electrolytes (Figure 2-15a,b), bare GO showed two redox couples which results from the redox reactions of carbon-oxygen functional groups. In neutral electrolytes (Figure 2-15c,d) distorted rectangular shapes are observed for GO with no distinct redox peaks signifying pseudocapacitive effects. Overall, much larger current densities are observed upon addition of metal cation. Enlarged current densities are reflected in the areal capacitance values as tabulated in Table 2-5. Accordingly, GO has the least contribution to Ni/GO composite followed by Fe/GO, Mn/GO, and Co/GO. After electrochemical reduction, capacitance values of GO enhanced due to increase in electrical conductivity. Thus, rGO contribution to the overall capacitance increased compared to that of GO (Figure 2-17). In fact, rGO has higher capacitance than the rMn/GO composite (Table 2-5). This behavior may be explained with the weakened interaction of Mn with GO layers compared

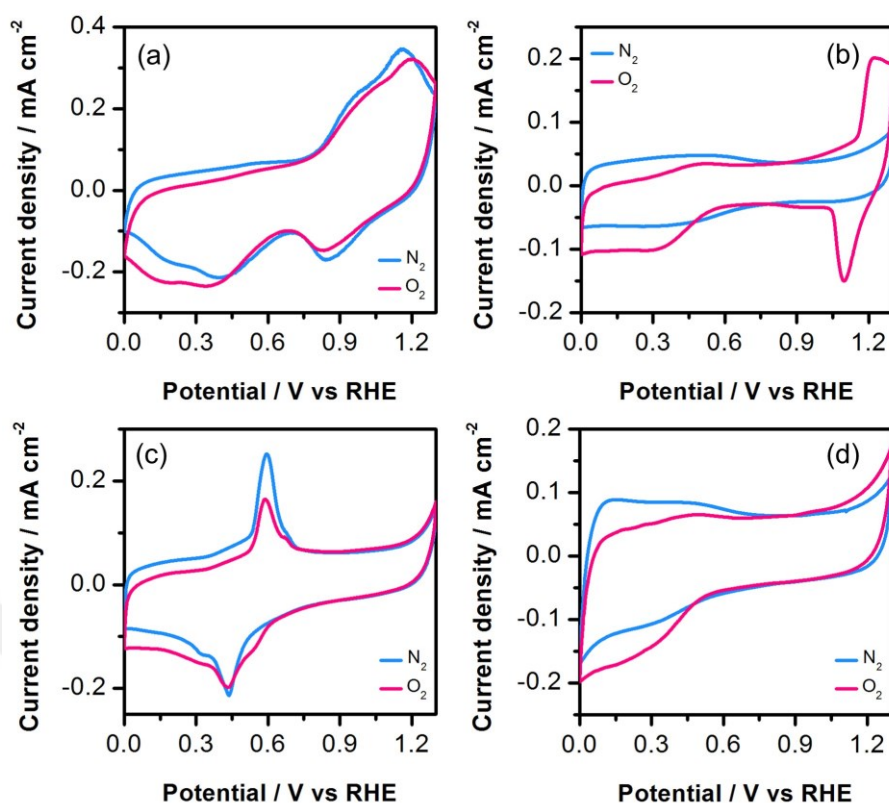


Figure 2-18 Cyclic voltammograms of (a) rCo/GO (b) rNi/GO (c) rMn/GO (d) rFe/GO in N₂ and O₂ saturated 0.1 M KOH. Scan rate: 50 mV s⁻¹.

to Mn with surrounding water molecules (hard acid-hard base interaction). After reduction, even lower amount of oxygen functional groups is present as anchoring points for the metal. As the CV measurement proceeds, manganese may be diffusing into the electrolyte solution slowly until no Mn (oxide) is left to contribute to the charge storage. To investigate the electrocatalytic properties of reduced metal/GO composites, CV measurements were conducted in N₂ and O₂ saturated 0.1 M KOH solution. rCo/GO exhibited similar redox peaks in both N₂ and O₂ saturated solutions (Figure 2-18a). rNi/GO had almost purely capacitive current in N₂ saturated solution, whereas the redox peaks arising from the formation of NiOOH from Ni(OH)₂ are observed when switching the purging gas to O₂ (Figure 2-18b). rMn/GO shows symmetric redox peaks which are probably due to transformation between Mn(OH)₂ and MnO₂ according to the Pourbaix diagram of manganese in the used pH and potential range (Figure 2-18c). [92] rFe/GO exhibited similar distorted rectangular shape voltammogram as in neutral electrolyte (Figure 2-18d). In all the voltammograms, a well-defined wave appears around 0.5-0.6 V (vs RHE) upon switching the

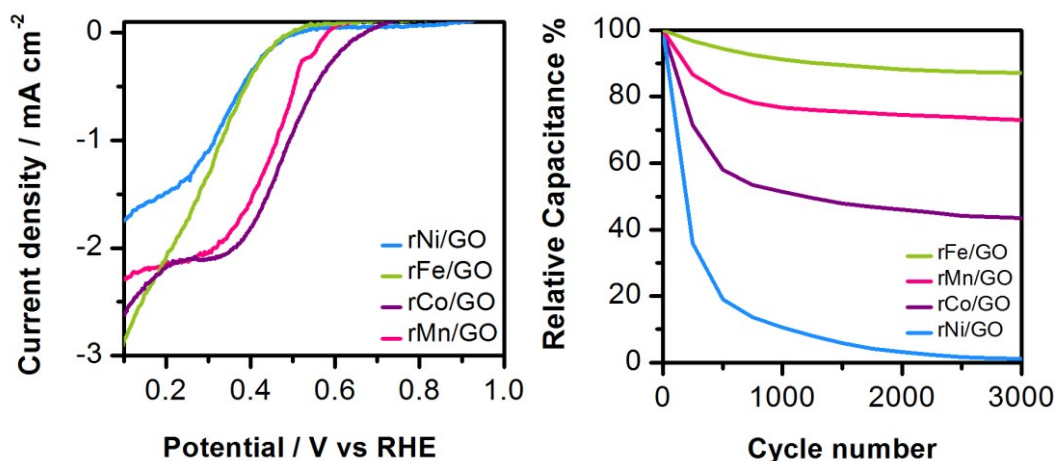


Figure 2-19 (a) ORR polarization curves of rMetal/GO in O₂ saturated 0.1 M KOH. Scan rate: 5 mV s⁻¹, rotation speed: 1600 rpm (b) Cyclic stability curves of rMetal/GO for 3000 cycles at 100 mV s⁻¹. rCo/GO and rNi/GO stability were conducted in 1 M KOH, rMn/GO and rFe/GO were conducted in 0.5 K₂SO₄ solutions

purging gas from N₂ to O₂ which suggests ORR taking place in that specific potential. [112] To analyze the electrocatalytic properties of composites towards ORR, RDE measurements were conducted. Figure 2-19a compares ORR polarization curves of reduced metal/GO composites at 5 mV s⁻¹. Calculated half wave-potentials are: 0.48, 0.38, 0.47, and 0.29 V for rCo/GO, rNi/GO, rMn/GO, and rFe/GO, respectively. Thus, the electrocatalytic activity towards ORR follows the trend: rCo/GO > rMn/GO > rNi/GO > rFe/GO.

Cyclic stability measurements of reduced metal/GO composites were conducted by CV measurements in the same electrolyte solutions used in capacitance calculations for each metal. Relative capacitance values are plotted against cycle number in Figure 2-19b. Accordingly, after 3000 cycles of CV, rFe/GO showed the highest stability (87 %) followed by rMn/GO (73 %), rCo/GO (44 %), and rNi/GO (1.1 %). The retention values of rFe/GO and rMn/GO are promising since these electrodes were prepared without any binders to improve the adhesion between the composite and the current collector. To understand the different stability responses of different metal cations, charge storage mechanisms of these composites were investigated by the analysis of the change in currents with sweep rate in CV measurements. [113] In this regard, the percentages of current arising from the capacitive and diffusion-limited processes are calculated according to the following processes and the values are given in Figure 2-20.

The current recorded at a fixed potential value can be expressed as:

$$I(V) = k_1 v + k_2 v^{1/2} \quad (2-6)$$

where I is the current density (mA cm^{-2}) at potential V , and v is scan rate in mV s^{-1} . The slope of the plot $I(V)/v^{1/2}$ vs $v^{1/2}$ enables calculation of k_1 , and the intercept gives k_2 . Thus, $k_1 v$ is the fraction of current arising from capacitive effects, and $k_2 v^{1/2}$ is from diffusion-limited processes. [113] At the scan rate of cyclic stability (100 mV s^{-1}), rFe/GO has the highest capacitive contribution to the overall capacitance resulting in the enhanced stability. rFe/GO is followed by rMn/GO , rCo/GO , and rNi/GO in terms of capacitive contribution, in agreement with the stability results. Thus, by utilization of the charge storage mechanism analysis info, cyclic stability of a metal/GO composite can be predicted. Upon increase in scan rate, diffusion-limited processes arises, reaching around

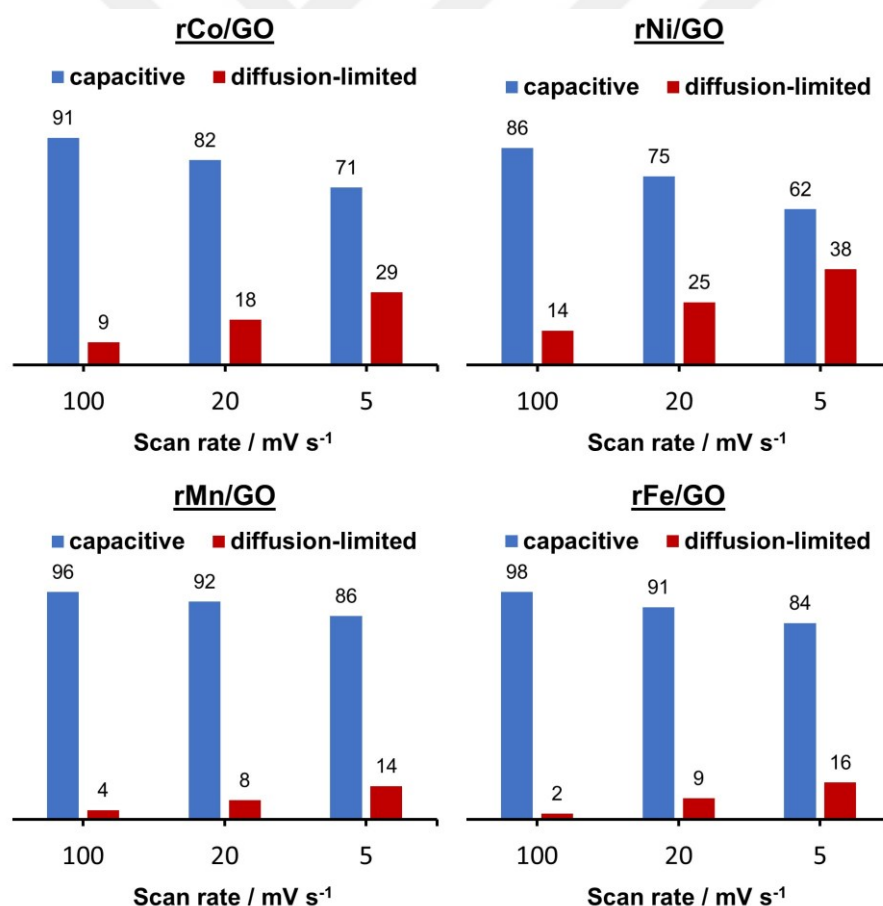


Figure 2-20 Charge storage mechanism analysis for all the reduced metal/GO

30% in rCo/GO and 40% in rNi/GO (Figure 2-20). In rMn/GO and rFe/GO, diffusion-limited processes remain lower indicating that these electrodes act almost as pure pseudocapacitors.

2.4. Conclusions

In this chapter, detailed characterization of GO synthesized via modified Hummers method is demonstrated. Single-layer GO nanosheets with lateral sizes in the range of micrometers were successfully synthesized and their presence was validated with AFM. The presence of oxygen functional groups was confirmed with XRD, XPS, and ATR-IR techniques. GO solution was combined with first-row transition metal cations by utilization of electrostatic interaction. From ICP-MS measurements, amount of metal bound to GO layers was determined in the following order: Fe>Co>Mn>Ni. ATR-IR spectra of metal/GO showed that the metal cation have strong affinity toward hydroxyl groups and C-OH end of carboxylic acids on GO layers. XPS results demonstrated that effective deoxygenation was obtained with electrochemical reduction technique. Additionally, metal cations remained in their divalent state in the as-deposited and reduced composites. XPS C1s spectra of metal/GO composites also validated that the metal cations prefer oxygen singly bound to carbon (C-O) rather than oxygen doubly bound to carbon (C=O) on GO nanosheets.

Electrodes of metal/GO composite were produced via simple drop-casting of metal/GO solutions onto HOPG current collectors. Electrochemical reduction resulted in enhancement of areal capacitance values around 16-fold in Co/GO and Mn/GO, whereas the values stayed nearly constant for Ni/GO and Fe/GO. Highest areal capacitance was achieved with Fe/GO (38.7 mF cm⁻²) followed by rCo/GO (31.6 mF cm⁻²) and rFe/GO (29.1 mF cm⁻²). Cyclic stability tests and the investigation of charge storage mechanisms showed that rMn/GO and rFe/GO had pseudocapacitive properties in neutral electrolyte. Electrochemical performance of rCo/GO and rNi/GO was restricted with diffusion-limited processes in alkaline electrolyte, resulting in lower cyclic stability.

Chapter 3: Layer-by-Layer Assembly of Metal (Hydr)oxide/Graphene Oxide Thin Films as Electrodes for Electrochemical Capacitors

3.1. Layer-by-Layer Assembled Nickel Hydroxide/Graphene Oxide Thin Films as Electrodes for ECs

3.1.1. Introduction

The energy density of the overall EC device is governed by the capacitance of individual electrodes. The capacitance of the electrodes can be improved by tuning the physiochemical characteristics of active material: increasing specific surface area to enhance contact with electrolyte, and boosting electrical conductivity to promote electron/ion diffusion from electrolyte to current collector.[114] Graphene, the sp^2 hybridized carbon network, has been exploited vastly as an EC material due to its remarkable electrical conductivity (2000 S cm^{-1}), high theoretical specific surface area ($2675 \text{ m}^2 \text{ g}^{-1}$), and specific capacitance (550 F g^{-1}). [71] For the improvement of the capacitance values of graphene, it is generally combined with transition metal/metal oxide nanoparticles since the latter possess large theoretical specific capacitance due to pseudocapacitive effects arising from reversible redox reactions. [115] As mentioned in Section 2.1. , there are various methods for production of graphene-metal composites. In this chapter, we utilize layer-by-layer assembly to create multilayered graphene-metal (hydr)oxide thin films as EC electrodes.

LBL assembly includes sequential adsorption of oppositely charged molecules which are attracted to each other via electrostatic, van der Waals forces, or hydrogen bonding. [116] LBL is a versatile and low cost technique that produces thin films with nanoscale uniformity and thus, have many application areas such as biosensors, batteries, field effect transistors, solar cells and supercapacitors. [117] The film thickness can be easily controlled by the number of deposition layers which directly affects the material properties. Up to date, various metal oxide/graphene or

carbon nanotubes (CNT) multilayers have been produced via LBL technique and exhibited excellent electrochemical properties. [118–121]

In this section, LBL assembly of $\text{Ni}(\text{OH})_2/\text{GO}$ thin film films are conducted via simple dip coating technique. $\text{Ni}(\text{OH})_2$ nanosheets used in this section is synthesized with a simple alkali precipitation method followed by exfoliation in water. Thin films are produced onto branched PEI modified ITO coated glass electrodes. The effect of film thickness on the surface topography is investigated with AFM measurements. To increase the electrical conductivity of the thin films, chemical reduction with hydrazine vapor was performed. The effect of chemical reduction on the surface chemistry is analyzed with XPS. CV and EIS measurements were performed for the evaluation of electrochemical performance as EC electrodes.

3.1.2. Materials & Methods

3.1.2.1. Materials

Graphite (natural, -200 mesh, 99.9995%), KOH (ACS reagent grade), K_2SO_4 (99%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98.0%), and NaNO_3 (99%) were purchased from Alfa Aesar. KMnO_4 , NaOH (>99.0%), and H_2O_2 (30%) were obtained from Merck Millipore. HCl (37%), H_2SO_4 (95-97%), and branched polyethyleneimine (bPEI, 50 wt% in water, avg. MW = 750,000) were obtained from Sigma Aldrich. Mercury/mercury oxide electrode (Hg/HgO , in 0.1 M KOH) was purchased from Radiometer Analytical SAS, France.

3.1.2.2. Synthesis of $\text{Ni}(\text{OH})_2$ Colloidal Solution

$\text{Ni}(\text{OH})_2$ aqueous colloidal solution was synthesized by a similar method reported by Schneiderová et al.[122]. Briefly, 3 mL 0.75 M NaOH was added to 5 mL 0.35 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution dropwise with an addition rate of 0.5 mL min^{-1} . Upon completion of addition, the solution was centrifuged at 8000 rpm for 5 min, followed by washing with distilled water 3 times. Washed precipitate was transferred to a 100 mL beaker, and 70 mL distilled water was added. The mixture was stirred for 20 h. After 20 h, clear green solution was obtained. To eliminate the aggregated

nanosheets, solution was centrifuged at 10000 rpm for 30 min and the supernatant solution was stored as $\text{Ni}(\text{OH})_2$ exfoliation solution.

3.1.2.3. Synthesis of Graphene Oxide

GO solution used in this chapter was synthesized via the same procedure explained in Section 2.2.2.

3.1.2.4. Production of $\text{Ni}(\text{OH})_2/\text{GO}$ Thin Films

$\text{Ni}(\text{OH})_2/\text{GO}$ thin films were deposited onto ITO coated glass (1 cm x 2 cm) substrates by an automated dip coater (KSV NIMA, multi vessel). Prior to LBL assembly of thin films, substrates were washed with acetone and ethanol by sonication, and washed with distilled water in between. Cleaned ITO substrates were dried with flowing N_2 . To obtain an active deposition area of 1 cm x 1 cm, substrates were covered with PTFE tape. The surface of freshly cleaned and dried substrates was modified via immersing them into 0.1 wt % bPEI solution for 15 min, followed by washing in distilled water for 5 min and air drying for 20 min. Then, bPEI modified ITO was dipped into freshly prepared $\text{Ni}(\text{OH})_2$ solution for 15 min, followed by washing and air drying. Finally, substrate was dipped into 0.2 mg mL^{-1} GO solution for 15 min, followed by washing and air drying. This completes 1 cycle of the dip coating process (without bPEI) and named as 1 bilayer of $\text{Ni}(\text{OH})_2/\text{GO}$. By repetition of cycles, films of desired thickness were obtained. The samples are named thereafter $[\text{Ni}/(\text{OH})_2/\text{GO}]_n$ (where n represents number of bilayer).

3.1.2.5. Chemical Reduction of $\text{Ni}/(\text{OH})_2/\text{GO}$ Thin Films

Reduction of LBL assembled films were carried out chemically with hydrazine vapor. Produced films were placed in a small glass vial in a vertical fashion, which were placed in a Schott type glass bottle. 100 μL of 98% $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was placed in between the glass vial and the outer bottle to ensure that the film was only exposed to the hydrazine vapor, not the liquid at ambient temperature. Each film was reduced in separate bottles. Prepared reduction bottles were placed into a drying oven, and the oven was kept at 90 $^\circ\text{C}$ for 10 h. After cooling down to room

temperature naturally, the films were taken out of the bottles and used without further treatment, including washing.

3.1.2.6. Structural Characterization of Ni(OH)₂/GO Thin Films

Atomic force microscopy (AFM) images of Ni(OH)₂/GO thin films were collected with Bruker Dimension Icon in ScanAsyst mode (tapping). For AFM, thin films deposited onto clean Si wafers were utilized. Average RMS roughness values were calculated using Nanoscope Analysis software. XRD diagram of produced Ni(OH)₂ powder was obtained with Bruker D2 Phaser with Cu K α source. Morphology of Ni(OH)₂ nanosheets were analyzed with FESEM coupled with a STEM detector.

3.1.2.7. Electrochemical Characterization of Ni(OH)₂/GO Thin Films

Electrochemical characterization of the films was conducted with a 3-electrode electrochemical setup connected to a potentiostat (Biologic VSP). ITO loaded with LBL films, Pt wire, and Hg/HgO (1 M KOH) was working, counter, and reference electrode, respectively. CV curves were recorded between scan rates of 100 to 5 mV s⁻¹. Electrochemical Impedance Spectroscopy (EIS) measurements were conducted with a potential amplitude of 10 mV in the frequency range 500 kHz-100 mHz.

3.1.3. Results & Discussion

3.1.3.1. Structural Characterization of Ni(OH)₂ Nanosheets

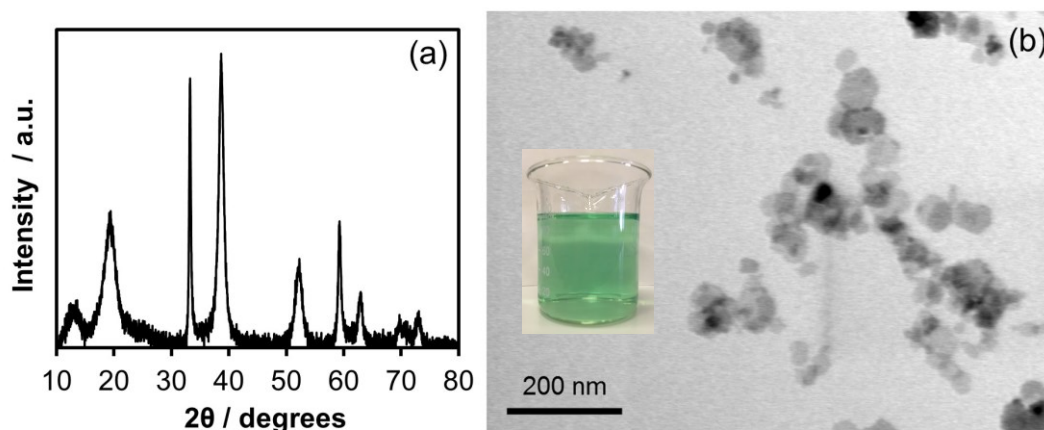


Figure 3-1 (a) XRD diagram (b) STEM image accompanied with digital image of Ni(OH)₂ nanosheets

After following the synthesis procedure in Section 3.1.2.2. , clear green exfoliation solution was obtained as shown in Figure 3-1b. To identify the crystal structure of obtained material, XRD was utilized. The peaks observed in XRD diagram matches with that of β -Ni(OH)₂ (JCPDS No: 14-0117). [123] STEM images in Figure 3-1b confirms the presence of hexagonally-shaped nanosheets with approximate lateral size of 50-100 nm.

3.1.3.2. Structural Characterization of Ni(OH)₂/GO Thin Films

AFM image of bPEI and 1-layer GO coated thin film is given in Figure 3-2a. In this image, overlapped wrinkled GO layers can be distinguished along with small humps which may be formed due to underlying bulky bPEI chains. Upon immersion of substrate to Ni(OH)₂ solution (Figure 3-2b), immediate deposition of hexagonal Ni(OH)₂ nanosheets was observed. The structure is dominated with Ni(OH)₂ nanosheets as the number of bilayers increased (Figure 3-2c,d). The average rms (root-mean-square) roughness value for the [Ni(OH)₂/GO]₁ thin film is calculated as 2.37 nm indicating the surface of the film is smooth. [118] Average rms roughness values increased

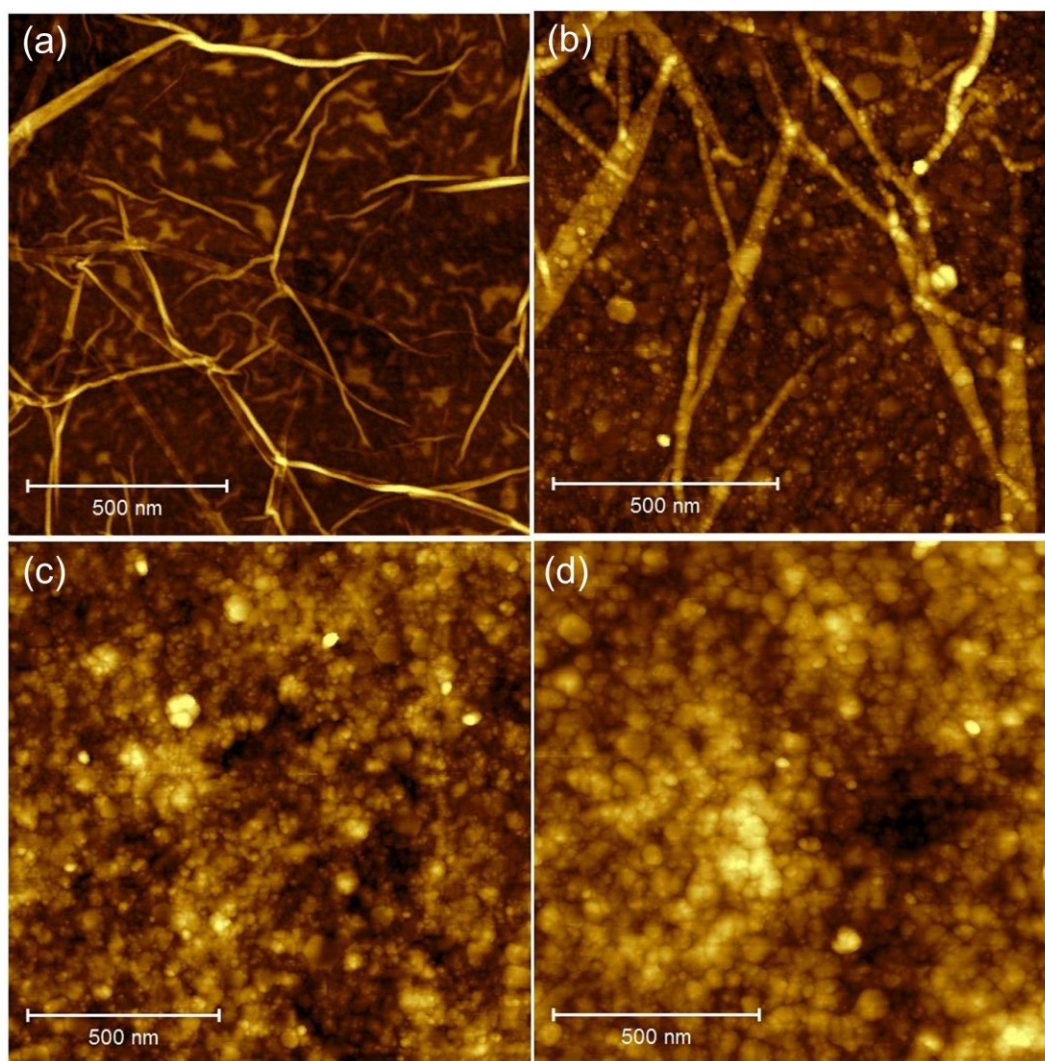


Figure 3-2 AFM images of (a) PEI/GO (b) $[\text{Ni}(\text{OH})_2/\text{GO}]_1$ (c) $[\text{Ni}(\text{OH})_2/\text{GO}]_5$ (d) $[\text{Ni}(\text{OH})_2/\text{GO}]_9$

slightly with number of bilayers: 3.01 and 3.85 nm for $[\text{Ni}(\text{OH})_2/\text{GO}]_5$, and $[\text{Ni}(\text{OH})_2/\text{GO}]_9$, respectively. Nevertheless, for 9 bilayer film has relatively low roughness showing that the deposition proceeds uniformly throughout the surface.

XPS was utilized to analyze the surface chemical structure of $\text{Ni}(\text{OH})_2/\text{GO}$ thin films. Figure 3-3a shows C 1s spectrum of $[\text{Ni}(\text{OH})_2/\text{GO}]_9$. The spectrum consists of three peaks at 284.4, 286.0, and 288.2 eV belonging to carbon-carbon, carbon singly bound to oxygen (hydroxyl, epoxy), and carbon doubly bound to oxygen (carbonyl and carboxyl), respectively. [16] All the aforementioned

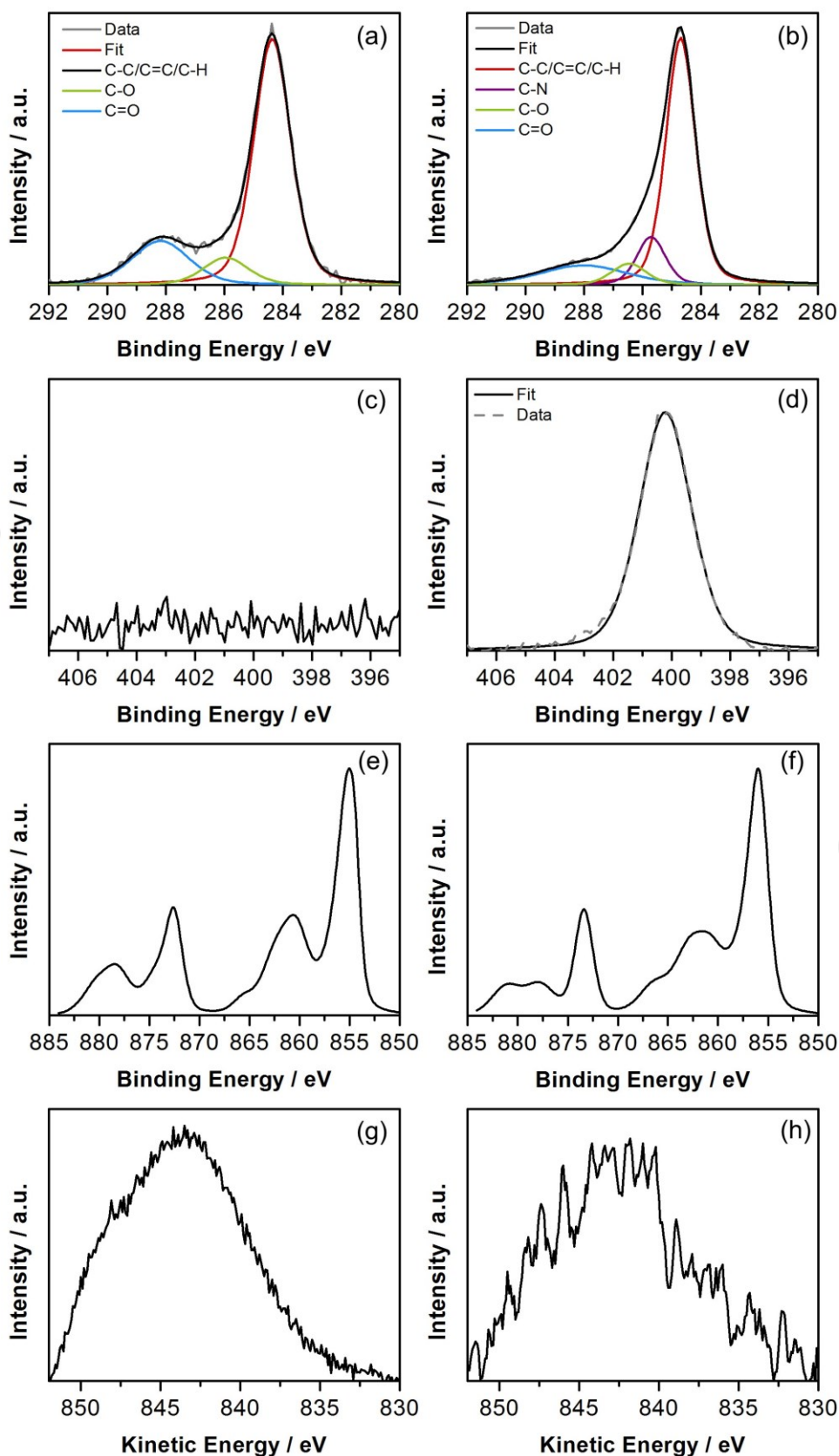


Figure 3-3 XPS C1s spectrum of (a) $[\text{Ni}(\text{OH})_2/\text{GO}]_9$ (b) $r[\text{Ni}(\text{OH})_2/\text{GO}]_9$, N1s spectrum of (c) $[\text{Ni}(\text{OH})_2/\text{GO}]_9$ (d) $r[\text{Ni}(\text{OH})_2/\text{GO}]_9$, Ni2p spectrum of (e) $[\text{Ni}(\text{OH})_2/\text{GO}]_9$ (f) $r[\text{Ni}(\text{OH})_2/\text{GO}]_9$, NiLMM spectrum of (g) $[\text{Ni}(\text{OH})_2/\text{GO}]_9$ (h) $r[\text{Ni}(\text{OH})_2/\text{GO}]_9$

peaks arise from the GO in the surface. After reduction, relative intensity of C-O and C=O peaks decreased (compared to C-C) indicating deoxygenation of GO (Figure 3-3b). Additionally, a peak appears around 285.7 eV pushing the C-O peak to higher binding energy which is associated with the formation of C-N bond. [124] Furthermore, while N1s spectrum of $[\text{Ni}(\text{OH})_2/\text{GO}]_9$ gave no detectable signal (Figure 3-3c), $r[\text{Ni}(\text{OH})_2/\text{GO}]_9$ exhibits a single peak at 400.2 eV (Figure 3-3d). The peak around 400 eV belongs to pyrrolic N, and evolution of this peak suggests nitrogen doping in the graphitic skeleton. [125] Ni 2p spectrum of $[\text{Ni}(\text{OH})_2/\text{GO}]_9$ showed $2p_{3/2}$ peak at 855.1 eV (Figure 3-3e). This binding energy value and the spectral feature matches with that of $\text{Ni}(\text{OH})_2$, while both remains also unchanged after reduction (Figure 3-3f). [126] To identify the atom(s) bound to the element of interest, utilization of Auger parameters is quite useful. [127–129] Auger parameter (α') is calculated according to the following equation:

$$\alpha' = E_k(\text{NiLMM}) + E_b(\text{Ni}2p_{3/2}) \quad (3-1)$$

where $E_k(\text{NiLMM})$ is the kinetic energy of the peak maximum in NiLMM spectrum, and $E_b(\text{Ni}2p_{3/2})$ is the binding energy of the peak maximum in Ni 2p spectrum. NiLMM spectrum of $[\text{Ni}(\text{OH})_2/\text{GO}]_9$ exhibits a broad peak centered around 843.5 eV, which results in an auger parameter of 1698.6 eV (Figure 3-3g). This value validates the $\text{Ni}(\text{OH})_2$ structure. [126] Auger parameter of $r[\text{Ni}(\text{OH})_2/\text{GO}]_9$ is calculated as 1698.4 eV indicating that the structure is unchanged.

3.1.3.3. Electrochemical Characterization of $\text{Ni}(\text{OH})_2/\text{GO}$ Thin Films

Figure 3-4a shows cyclic voltammograms of $[\text{Ni}(\text{OH})_2/\text{GO}]$ thin films from bilayers 1 to 9 at 20 mV s^{-1} . $[\text{Ni}(\text{OH})_2/\text{GO}]_1$ exhibited the lowest current, whereas higher bilayer numbers had similar current densities (capacitances). Reducing the films with hydrazine enhanced the current densities almost 3-fold due to increased electrical conductivity of GO layers with deoxygenation (Figure 3-4b). Observed current densities increased with the number of bilayers, where $[\text{Ni}(\text{OH})_2/\text{GO}]_3$ and $[\text{Ni}(\text{OH})_2/\text{GO}]_5$ showed similar voltammograms. Figure 3-4c,d show cyclic voltammograms

of $[\text{Ni}(\text{OH})_2/\text{GO}]_9$ and $r[\text{Ni}(\text{OH})_2/\text{GO}]_9$ at different scan rates. A couple of redox peaks is observed assigned to the redox peaks of $\text{Ni}(\text{OH})_2$ in alkaline solutions [130]:

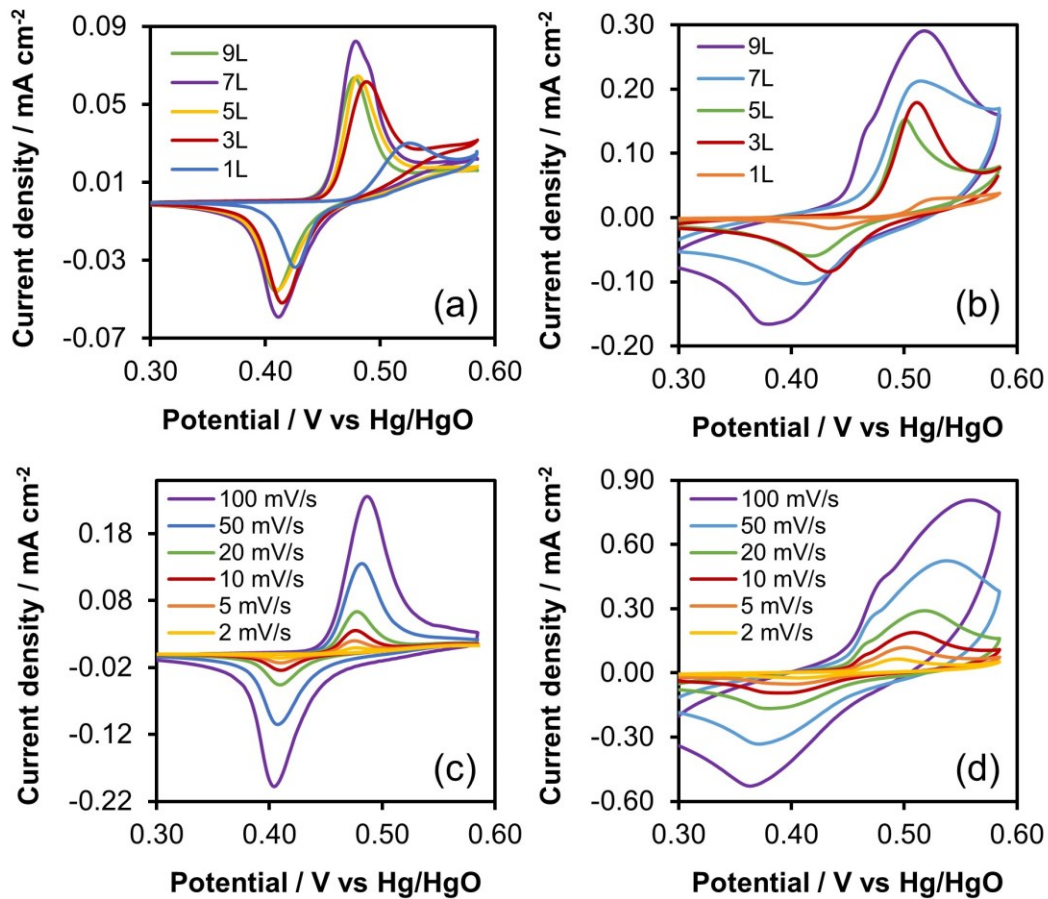
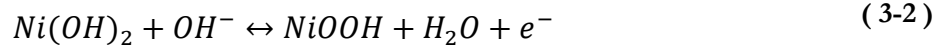


Figure 3-4 Cyclic voltammograms of (a) $[\text{Ni}(\text{OH})_2/\text{GO}]$ (b) $r[\text{Ni}(\text{OH})_2/\text{GO}]$ from bilayers 1 to 9, (c) $[\text{Ni}(\text{OH})_2/\text{GO}]_9$ (d) $r[\text{Ni}(\text{OH})_2/\text{GO}]_9$ at different scan rates

Reduced films showed broader peaks along with higher current densities resulting in higher capacitance values (Figure 3-4d). Figure 3-5 shows areal capacitance values of $[\text{Ni}(\text{OH})_2/\text{GO}]$ thin films with different layer numbers. As the voltammograms previously implied, except $[\text{Ni}(\text{OH})_2/\text{GO}]_1$, all bilayers have similar areal capacitance values (Figure 3-5a). As the scan rate decreases, gradual increase in areal capacitance is observed due to diffusion-limited processes. [36] After reduction, increase in areal capacitance observed with the number of bilayers, and

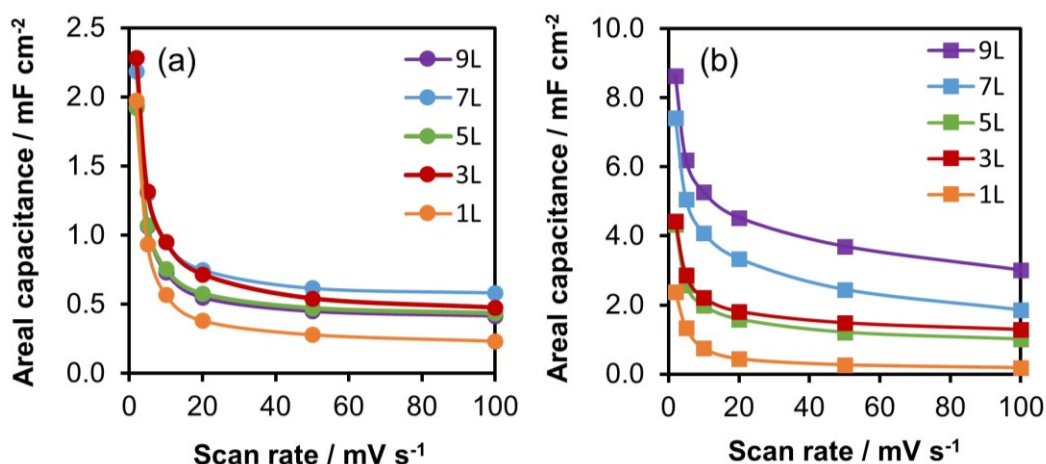


Figure 3-5 Areal capacitance vs scan rate curves for (a) [Ni(OH)₂/GO] (b) r[Ni(OH)₂/GO] from bilayers 1 to 9

r[Ni(OH)₂/GO]₉ achieved almost 3-fold higher capacitance value than the as-deposited counterparts (Figure 3-5b). r[Ni(OH)₂/GO]₉ had areal capacitance of 8.6 mF cm⁻² at 2 mV s⁻¹ which is retained as 3.0 mF cm⁻² at 100 mV s⁻¹. Thus, r[Ni(OH)₂/GO]₉ exhibited 3-fold higher areal capacitance value than LBL assembled Co-Al LDH/rGO thin films when compared at the same scan rate. [118]

The charge storage mechanisms of Ni(OH)₂/GO thin films were analyzed by following the calculations explained in Section 1.2.1.3.4. The anodic and cathodic peak currents are measured for different scan rates and plotted as log_i vs log_v in Figure 3-6. The slope gives the b-value, which is 1.0 for purely capacitive electrodes, and 0.5 for diffusion-limited processes. [113] For

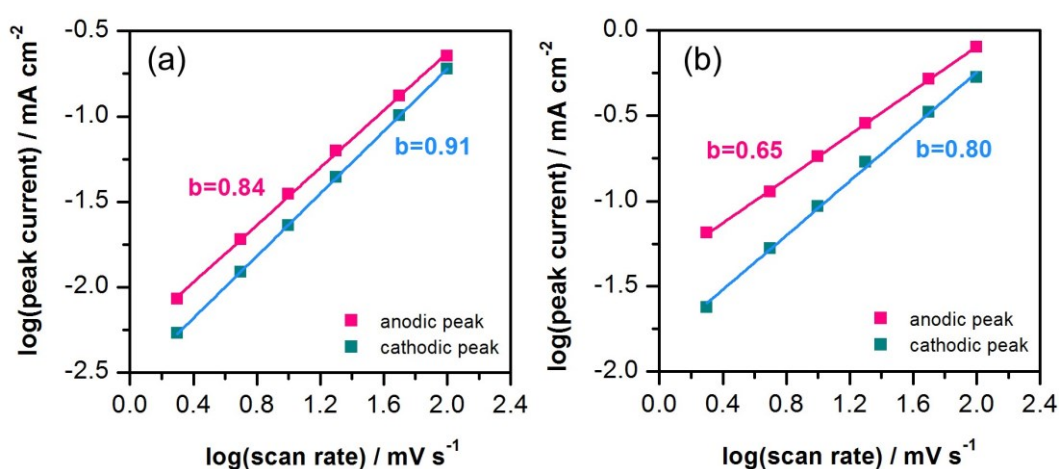


Figure 3-6 Log(current density) vs log(scan rate) plots for (a) [Ni(OH)₂]₉ and (b) r[Ni(OH)₂]₉

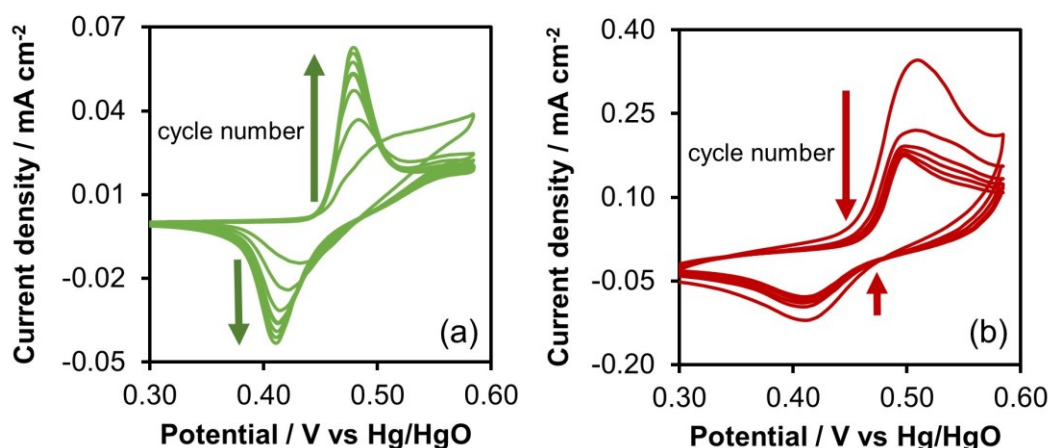


Figure 3-7 Change of voltammograms during initial cycles of CV for (a) $[\text{Ni}(\text{OH})_2/\text{GO}]_5$ and (b) $r[\text{Ni}(\text{OH})_2/\text{GO}]_5$

$[\text{Ni}(\text{OH})_2/\text{GO}]_9$, b-value is 0.84 for the anodic peak and 0.91 for the cathodic one, which are both fairly close to 1.0. Reducing the films with hydrazine causes decrease in b-values as shown in Figure 3-6b, especially for the anodic peak. Thus, as-deposited films exhibited more pseudocapacitive behavior, whereas hydrazine-reduction resulted in formation of a charge storage controlled with diffusion. Furthermore, when the initial CV curves are analyzed, the peak current of $[\text{Ni}(\text{OH})_2/\text{GO}]_5$ increased steadily whereas a substantial decrease is observed in $r[\text{Ni}(\text{OH})_2/\text{GO}]_5$ (Figure 3-7). The reason for this behavior can be explained with the stronger interaction between oxygen functional groups of GO and $\text{Ni}(\text{OH})_2$ particles. The remained functional groups in reduced GO layers result in less binding sites for metal hydroxides. Impedance measurements were conducted to further investigate the charge storage characteristics of LBL assembled thin films. Bode plot of $[\text{Ni}(\text{OH})_2/\text{GO}]$ thin film showed that the maximum phase angle reaches almost -90° at lower frequency limit which is typically observed in ideal capacitors (Figure 3-8). [131] The maximum phase angle observed in reduced film is around -60° indicating less capacitive and more diffusion-limited characteristics, in agreement with the b-value analysis. Furthermore, relaxation time constants (τ_0) are calculated from conversion of the frequency at -45° ($\tau=1/f$). τ_0 are calculated as 2.92 and 5.70 ms for as-deposited and reduced films, respectively. Both values are comparable with that of carbon microcapacitors reported in the literature. [132]

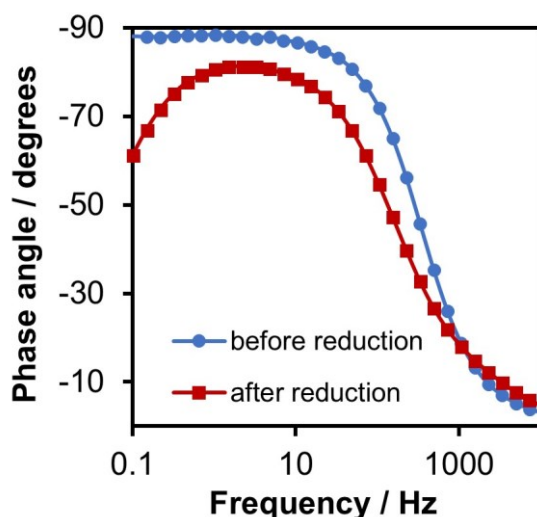


Figure 3-8 Bode plots of $[\text{Ni}(\text{OH})_2/\text{GO}]$ thin film before and after chemical reduction with hydrazine

3.1.4. Conclusions

In this section, we introduced LBL-assembled $\text{Ni}(\text{OH})_2/\text{GO}$ thin films as possible electrodes for ECs. $\text{Ni}(\text{OH})_2$ nanosheets used in the multilayered film was synthesized by a facile alkali precipitation of nickel(II) salt with NaOH followed by exfoliation in water. Obtained nanosheets were combined with GO nanosheets in a layer-by-layer fashion by simple dip-coating process. The surface topography of $\text{Ni}(\text{OH})_2/\text{GO}$ thin films were monitored with AFM. For the increase in electrical conductivity of the thin films, chemical reduction with hydrazine vapor was utilized. XPS results showed that GO in the multilayered film was deoxygenated and nitrogen doped simultaneously during hydrazine treatment, whereas $\text{Ni}(\text{OH})_2$ structure was unaffected.

Produced thin films were characterized as possible electrodes for ECs. The areal capacitance values were tuned between 0.4 and 4.5 mF cm^{-2} by increasing the bilayer number from 1 to 9. The variation of peak currents with scan rates revealed that as-deposited films had pseudocapacitive properties, whereas reduced films' charge storage were limited by diffusion. This behavior was also reflected in EIS measurements.

3.2. Layer-by-Layer Assembled Superparamagnetic Iron Oxide

Nanoparticles/Graphene Oxide Thin Films as Electrodes for Electrochemical Capacitors

This section includes a collaborative work between research groups of Assoc. Prof. Dr. Uğur Ünal, Dr. Emre Erdem from Institute of Physical Chemistry, University of Freiburg, and Assoc. Prof. Dr. Funda Yağcı Acar of Chemistry Department, Koç University.

3.2.1. Introduction

Among various transition metal oxides, iron oxides are attractive candidates as pseudocapacitors with their abundance, low cost, and environmental friendliness. [110] Unlike other phases of iron oxides, magnetite (Fe_3O_4) has electrical conductivity as a result of electron hopping between Fe^{2+} and Fe^{3+} ions in octahedral sites. [133]

There are several studies including LBL assembly of iron oxide/graphene thin films and their applications as EC electrodes. For instance, LBL grown 30 bilayer Fe_3O_4 /reduced graphene oxide (rGO) thin films had specific capacitance of 151 F g^{-1} at current density of 0.9 A g^{-1} in 1 M NaCl electrolyte. [134] Another study produced Fe_3O_4 /few layer graphene (FLG) multilayers via spin coating onto gold electrode with poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) layer as binder between gold and multilayers. [135] 15 bilayer Fe_3O_4 /FLG reached specific capacitance of 153 F g^{-1} at 0.1 A g^{-1} in $0.5 \text{ M Na}_2\text{SO}_3$.

In this section, layer-by-layer assembled superparamagnetic iron oxide nanoparticles (SPION)/GO hierarchical structures via simple dip coating technique are reported. Small cationic SPION coated with APTMS are used directly onto indium tin oxide (ITO) substrates without any binders or conductive additives. Chemical reduction of multilayers was conducted using hydrazine vapor to enhance electrical conductivity of GO. The effect of hydrazine-reduction on the structure of the multilayered films was investigated by atomic force microscopy (AFM) and X-ray

photoelectron spectroscopy (XPS). Electrochemical performance of the films was evaluated with cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. Defect structures and the oxidation state of Fe ions were investigated via state-of-the-art electron paramagnetic resonance (EPR) spectroscopy.

3.2.2. Materials & Methods

3.2.2.1. Materials

All the chemicals were used as received without further purification. Graphite (natural, - 200 mesh, 99.9995 %) and NaNO_3 (99 %) were obtained from Alfa Aesar. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, KMnO_4 and H_2O_2 (30 %) were purchased from Merck Millipore. Ammonium hydroxide (26 %), H_2SO_4 (95-97 %) and HCl (37 %) were obtained from Sigma Aldrich. (3-aminopropyl) trimethoxysilane and Amicon filters (PES, 10K) were purchased from Gelest (Germany) and Sartorius AG (Germany), respectively. All the solutions used in this study were prepared with doubly distilled water. Saturated calomel electrode (SCE, in saturated KCl) was purchased from Radiometer Analytical SAS, France.

3.2.2.2. Synthesis of Graphene Oxide

GO used in this study was synthesized as explained in Section 2.2.2.

3.2.2.3. Synthesis of (3-Aminopropyl) trimethoxysilane (APTMS) Coated SPION

The synthesis and characterization of APTMS coated SPION was performed in the Polymers and Nanomaterials Research Laboratory of Assoc. Prof. Funda Yağcı Acar in Koç University. APTMS coated SPION were synthesized through aqueous coprecipitation of ferric and ferrous salts under alkaline conditions and with the silanization process of APTMS on the nanoparticles. Initially, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were mixed under argon atmosphere and then degassed NH_4OH and APTMS were injected to reaction medium during the mixing. The molar ratio between the precursors is $[\text{APTMS}]:[\text{Fe}^{2+}+\text{Fe}^{3+}]:[\text{OH}] = 0.8 : 1 : 15$. The reaction was carried out for 1 h at 80

°C. Then, the mixture was cooled down naturally while mixing and standing on a 0.3 T magnet overnight to precipitate coalesced particles. The colloidal suspension after magnetic precipitation was collected and purified with ultracentrifugal filtration (Amicon PES filter, 10K).

3.2.2.4. Layer-by-Layer Assembly of SPION/GO Thin Films

For the electrochemical characterization, SPION/GO films were deposited onto ITO coated glass (10 mm x 20 mm) substrates by an automated dip coater (KSV NIMA, multi vessel). The substrates were first cleaned by sonication in acetone, water, ethanol, and water, respectively. Prior to dip coating, ITO substrates were covered with polytetrafluoroethylene (PTFE) tape to get an active deposition area of 1 cm². Freshly cleaned ITO substrates were first immersed into APTMS coated SPION solution (0.5 mg mL⁻¹) for 15 min, followed by washing in distilled water three times (each washing was 1 min), and air-drying for 20 min. The substrates were then immersed into GO solution (0.5 mg mL⁻¹) for 15 min, followed by washing and air-drying for 20 min. This completes one cycle of dip coating process and creates one bilayer of film. This cycle was repeated in order to create 1,3,5,7, and 9 bilayers in this work (named thereafter [SPION/GO]_n, where n is the number of bilayers).

3.2.2.5. Structural Characterization of SPION/GO Thin Films

Atomic force microscopy (AFM) images of SPION/GO thin films were collected with Bruker Dimension Icon in ScanAsyst in tapping mode. For AFM, thin films deposited onto clean Si wafers were utilized. Average RMS roughness values were calculated using Nanoscope Analysis software. Zeta potential measurements of APTMS coated SPION and GO solutions (same concentration with the dip coating, 0.5 mg mL⁻¹) were conducted with Malvern ZS Zetasizer. Scanning transmission electron microscopy (STEM) images of SPION/GO films were measured with field emission scanning electron microscopy (FESEM, ZEISS UltraPlus) coupled with a STEM detector. For the analysis, 1 bilayer of SPION/GO was coated onto STEM grid (specification) via dip coating. Transmission electron microscopy (TEM) images of SPION were taken with Techani

G2 F30 at 200 kV acceleration voltage in National Nanotechnology Research Center (UNAM), Bilkent University. SPION samples were prepared on a carbon coated Cu-grid from a dilute solution. For UV measurements, same dip coating process was conducted onto quartz substrates (10 mm x 20 mm). Prior to deposition, quartz was cleaned exactly the same way with that of ITO. After each bilayer, dried film was placed into a special film holder in UV-Vis spectrophotometer (Shimadzu UV-3600). The baseline for UV-Vis measurements was taken with two clean quartz substrates placed into reference and sample holders. UV-Vis spectra were measured between 200-600 nm. For Quartz Crystal Microbalance (QCM) measurements, SRS QCM 100 system was utilized. Same dip coating procedure was applied using QCM crystals (5 MHz 1-inch Au-coated crystals obtained from Phillip Technologies, LLC, SC, USA,) as substrates. The crystals were treated with freshly prepared piranha solution three times followed by washing with water in ultrasonic bath (*Caution! Piranha solution is extremely reactive and must be handled with extreme caution; use the smallest possible volume*). Prior to dip coating, quartz was covered with parafilm to expose only the front side of the crystal to the solution. Thus, there was coating only on one side. After each layer, dried crystals were placed into QCM holder and frequency was recorded until a stable signal was obtained. XPS measurements were conducted with Thermo K-Alpha Spectrometer with an Al K α source. For the analysis, films deposited onto Si wafers were utilized. The fittings for the experimental data were done with Advantage software. All the atomic percentages reported in this study were calculated from the fittings of region spectra.

3.2.2.6. Chemical Reduction of SPION/GO Thin Films

Reduction of LBL assembled films were carried out exactly with the same procedure explained in Section 3.1.2.5.

3.2.2.7. Electrochemical Characterization of SPION/GO Thin Films

A conventional three-electrode electrochemical cell connected to a potentiostat/galvanostat (Biologic VSP) was utilized for all the electrochemical characterization. The working electrode was the produced LBL films onto ITO, the counter electrode was a platinum wire, and the reference

electrode was SCE (in saturated KCl) connected to the cell via an agar salt bridge (prepared in 3.5 M KCl). The electrolyte solution for all measurements was 0.5 M K₂SO₄. The potential values are reported with respect to Ag/AgCl (in saturated KCl) electrode for simpler comparison with the literature. In cyclic voltammetry (CV) measurements, films were scanned between 0.0 and -0.8 V (vs Ag/AgCl (in saturated KCl)) at scan rates ranging from 100 to 5 mV s⁻¹. Cyclic stability tests were conducted in the same potential range with scan rate of 100 mV s⁻¹. Electrochemical impedance measurements were conducted with potential amplitude of 10 mV in the frequency range 500 kHz-100 mHz.

3.2.2.8. Electronic Characterization of SPION/GO Thin Films via EPR spectroscopy

EPR measurement and analysis were performed by Dr. Emre Erdem in University of Tours. The X-band (microwave frequency 9.86 GHz) spectra were measured at room temperature by EMX-plus spectrometer with high-Q Bruker resonator. The offset in the magnetic field and the exact g-factors in X-band measurements were determined with a polycrystalline DPPH (2-diphenyl-1-picrylhydrazyl) reference sample of well-known g-factor ($g=2.0036$). The EPR spectral analysis has been performed using the WINEPR program from Bruker. The following EPR experimental parameters were used: microwave power: 2 mW; modulation amplitude: 1 G; time constant: 81 ms; receiver gain: 2×10^3 .

3.2.3. Results & Discussion

3.2.3.1. Structural Characterization of SPION/GO Thin Films

LBL assembly of SPION/GO layers resulted in slightly brown colored thin films that are barely visible to naked eye. The films became visible after chemical reduction with hydrazine vapor and the color turned to dark gray, in which the intensity of the color increased with the number of bilayers, as expected (see Figure 3-9b for the digital images). The homogeneity of the deposition is apparent even from the physical appearance of the films. Figure 3-9c-e shows STEM images of

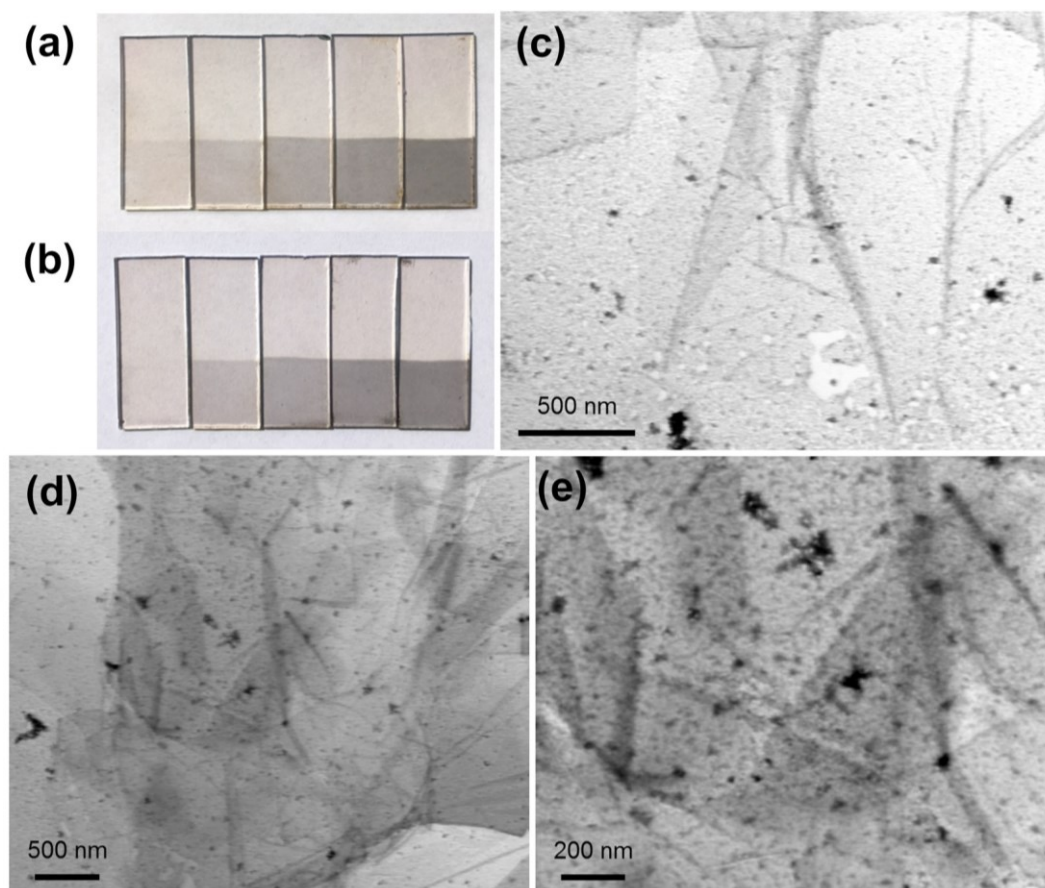


Figure 3-9 Digital images of (a) SPION/GO thin films after CV measurement from bilayers 1 to 9 (b) r[SPION/GO] from bilayers 1 to 9, (c-e) STEM images of [SPION/GO]₁

1L SPION/GO. Single GO layers decorated with SPION are visible; SPION are highly dispersed on GO with a few aggregated nanoparticles.

During formation of LBL assemblies, no polyelectrolyte was used to bind the structures to the substrates. First, cleaned ITO substrates were immersed in APTMS coated SPION solution, which resulted in a positively charged surface due to the positive zeta potential of SPION (+38.5 mV). Negatively charged GO layers (-43.2 mV) was deposited onto SPION layers via electrostatic interaction. LBL assembly was tracked with UV-vis spectroscopy. Figure 3-10a shows UV-vis spectra for the bilayers from 1 to 9. The peak around 230 nm is attributed to $\pi \rightarrow \pi^*$ of aromatic C=C bonds accompanied by a broad shoulder around 300 nm which arises from $n \rightarrow \pi^*$ transitions of C=O bonds. [136] These two features prove the existence of GO in the multilayered film

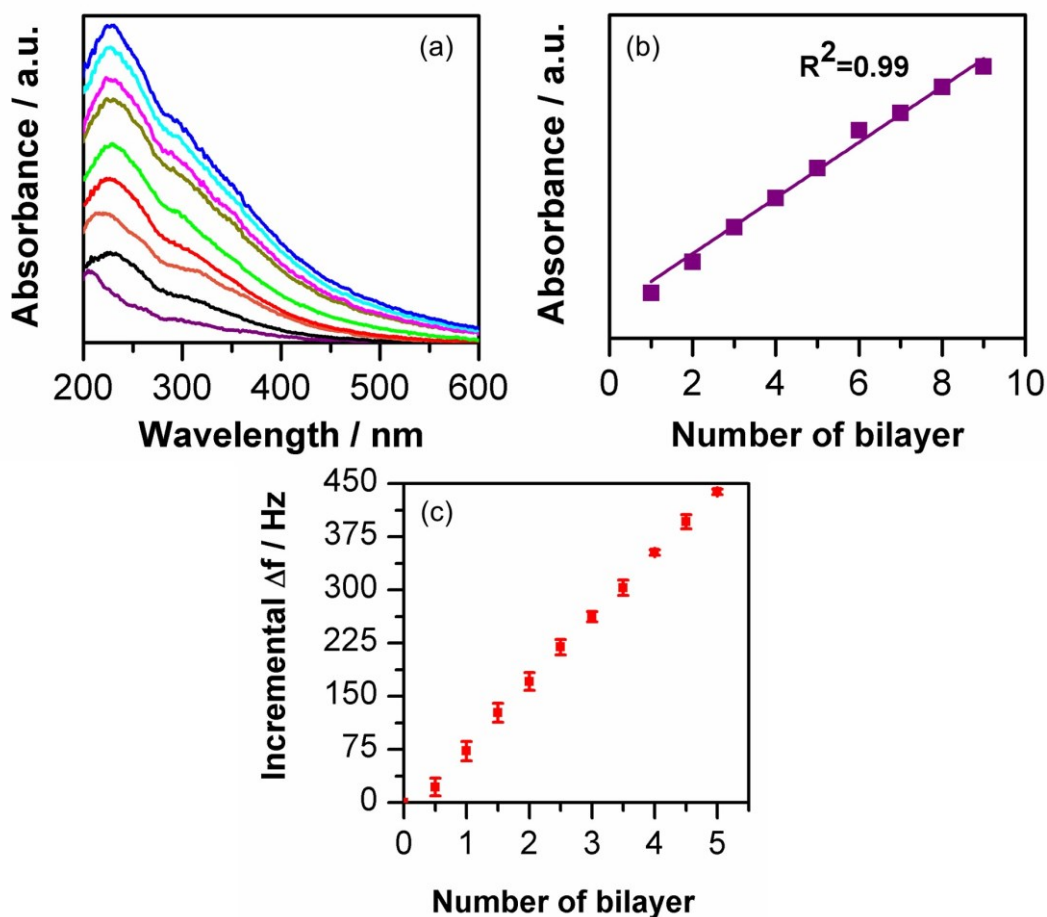


Figure 3-10 (a) UV-Vis spectra of SPION/GO thin films from bilayers 1 to 9. (b) Absorbance at 230 nm change with bilayer number. (c) Incremental frequency change with number of bilayers during QCM measurements.

(Figure 3-11a). The absorbance of the films increases linearly with the number of bilayers (Figure 3-10b) which shows the interaction between SPION and GO layers. Also, presence of shoulder around 350 nm shows successful incorporation of SPION in between GO layers since UV-vis spectrum of SPION solutions displays a broad band at 300-400 nm which is attributed to charge transfer transition between Fe^{3+} -O (octahedral) and Fe^{3+} - Fe^{2+} (tetrahedral) sites (Figure 3-11b). [134]

QCM is a powerful tool to quantify the thickness/mass of thin film deposits. By using QCM, it is possible to detect mass changes around few nanograms/ cm^2 by measuring frequency changes in the deposits. [137] The mass of the deposited layers can be calculated by using the following modified Sauerbrey equation [137]:

$$\Delta f = -C_f \times \Delta m \quad (3-3)$$

Where Δf is the change in frequency, C_f is the sensitivity factor ($56.6 \text{ Hz.cm}^2 \mu\text{g}^{-1}$ for 5 MHz gold coated crystal), and Δm is the mass change per unit area in g cm^{-2} . QCM measurements were conducted after each dried layer of SPION or GO, and by exactly mimicking the dip coating procedure. Figure 3-10c shows the incremental frequency change with respect to number of layers. The frequency increases linearly with the number of bilayers, in agreement with the UV-vis measurements. Each SPION layer results in average frequency shift of $42 \pm 12 \text{ Hz}$ (corresponds to $0.737 \pm 0.206 \mu\text{g}$), and each GO layer results in average frequency shift of $46 \pm 4 \text{ Hz}$ (corresponds to $0.812 \pm 0.069 \mu\text{g}$). Thus, similar amount of SPION and GO deposits in each cycle from solutions with equal concentration (0.5 mg mL^{-1}). After chemical reduction with hydrazine, the mass of 9 bilayer film was reduced by 9.7 %.

AFM was utilized to evaluate the surface topography of SPION/GO films. Figure 3-12a shows $5 \mu\text{m} \times 5 \mu\text{m}$ scan size AFM image of $[\text{SPION/GO}]_9$. It is clear from the image that all the surface is covered with SPION and GO layers. In fact, wrinkles and edges of individual graphene sheets are visible. When higher magnification images are analyzed, nanoparticle assemblies in same regions can be seen (Figure 3-12d-f). Average root-mean-square (rms) roughness of $[\text{SPION/GO}]_9$ is calculated as $2.84 \pm 0.31 \text{ nm}$ indicating the surface of coating is smooth.[118]

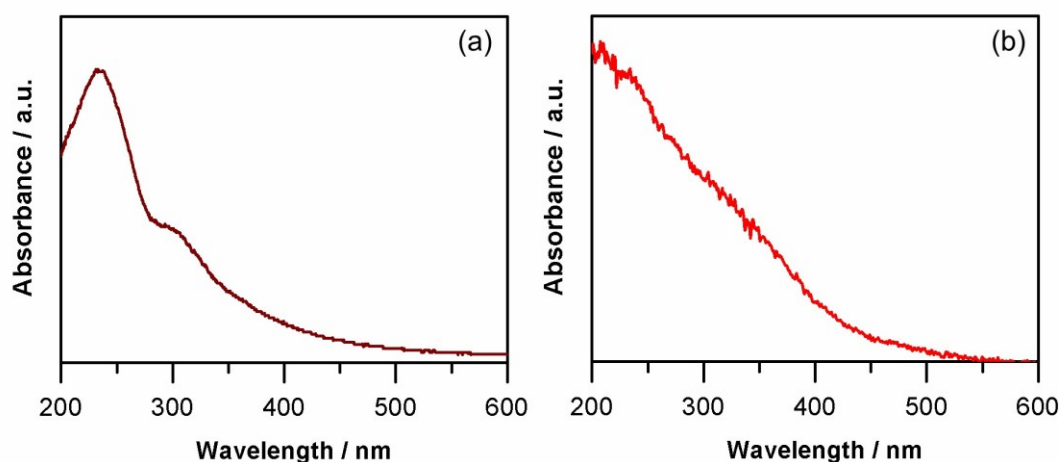


Figure 3-11 UV-Vis spectrum of (a) GO and (b) SPION solutions

After hydrazine reduction, there was a slight decrease in rms roughness value (2.20 ± 0.31 nm), which may be due to removal of functional groups from GO and restoration of the planar structure.

XPS was utilized to characterize the surface chemistry of the LBL films. Figure 3-13a shows C 1s spectrum of [SPION/GO]₉. Two peaks observed in C 1s spectrum were deconvoluted into three peaks: carbon-carbon/carbon-hydrogen (C-C/C=C/C-H), hydroxyl/epoxide (C-OH, C-O-C), and carbonyl/carboxyl groups (>C=O, -O-C=O) around 284.4, 286.4, and 288.2 eV, respectively. [16,138] These peaks are all belong to GO in the layered structure. N1s spectrum of [SPION/GO]₉ consists of two peaks at 399.3 and 401.2 eV, which correspond to -NH₂ and -NH₃⁺ bonds arising from the APMTS coating of iron oxide in the structure (Figure 3-13c). [139] Fe 2p spectrum of [SPION/GO]₉ contains 2p_{3/2} and 2p_{1/2} doublets located around 710.9 and 724.4 eV which are accompanied with broad shoulders. These binding energy values reveal that iron is present in a mixed oxidation state of +2 and +3 (Figure 3-13e). [105] Thus, the peak at 709.7 eV is assigned to Fe²⁺, and two peaks at 710.6 and 712.0 eV are to Fe³⁺. The broad shoulder contains Fe²⁺ and Fe³⁺

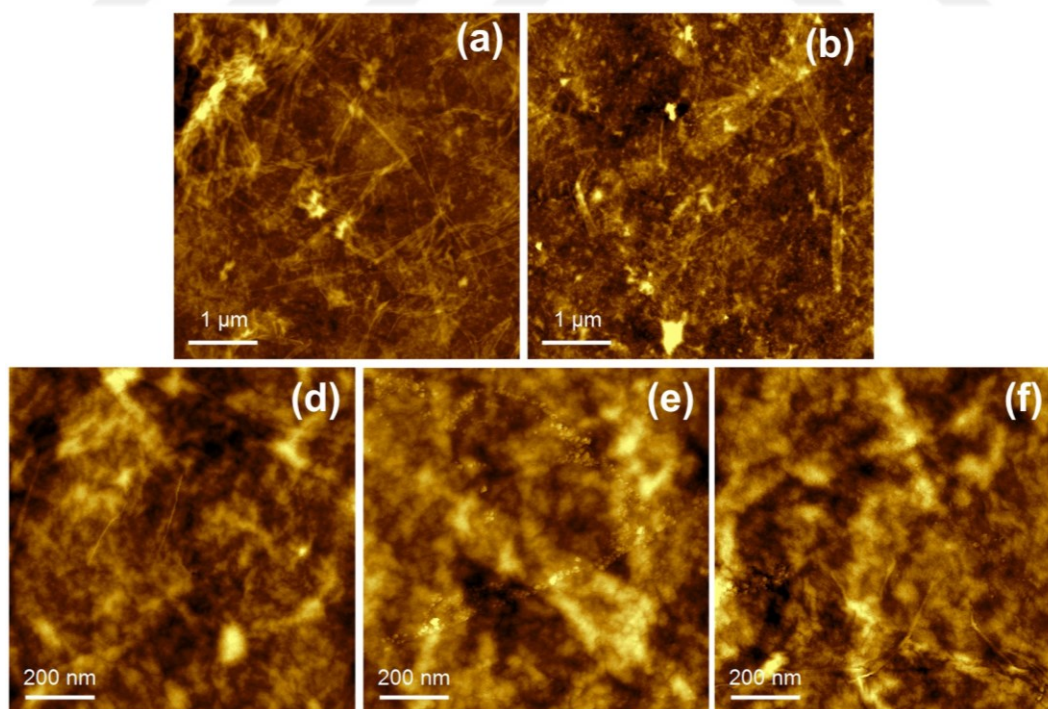


Figure 3-12 AFM image of (a) [SPION/GO]₉ (b) r[SPION/GO]₉. High magnification AFM images of [SPION/GO]₉

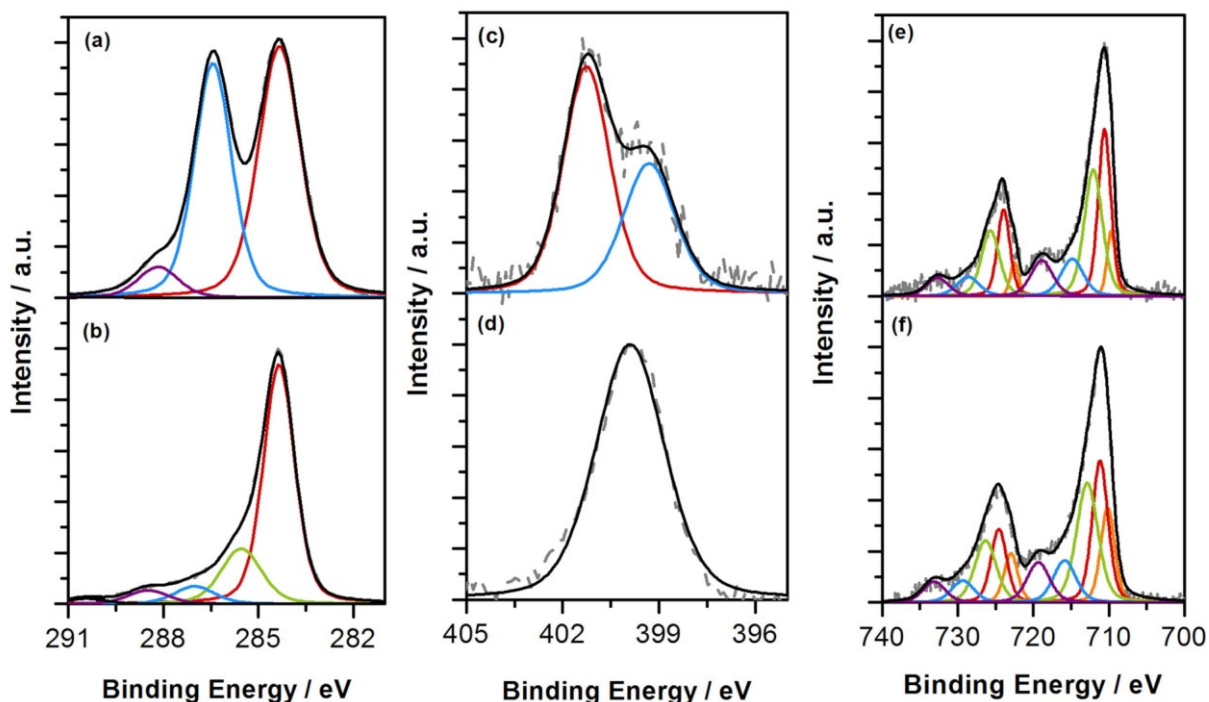


Figure 3-13 XPS C1s spectrum of (a) [SPION/GO]₉ (b) r[SPION/GO]₉, N1s spectrum of (c) [SPION/GO]₉ (d) r[SPION/GO]₉, Fe2p spectrum of (e) [SPION/GO]₉ (f) r[SPION/GO]₉

satellites around 714.9 and 718.9 eV. The presence of two oxidation states and their corresponding satellites validates the structure of iron oxide as Fe_3O_4 . [140,141] Overall, [SPION/GO]₉ surface contains 63.5% C, 33.0% O, 1.7% N, and 1.8% Fe (percentages are atomic). The ratio of C:O is slightly higher than that of GO reported in the literature [14] which is expected since oxygen originating from the Fe_3O_4 also contributes to the overall oxygen signal. After chemical reduction of [SPION/GO]₉ with hydrazine vapor for 10 h, significant decrease in oxygen functional groups is observed in C1s spectrum (Figure 3-13b). The decrease in functional groups is an indication of deoxygenation of GO. Two additional peaks are added to the fitting of C 1s spectrum of r[SPION/GO]₉ around 285.5 eV to account for the formation of C-N bonds, and 290.4 eV for the π - π^* satellite. [142] The incorporation of N into the graphene structure is further investigated with N1s spectrum (Figure 3-13d). The two peaks observed in the as-produced film transformed into a single peak centered around 399.9 eV. This peak is generally observed in hydrazine-reduced graphene oxides and indicates formation of pyrazoline groups. [21] Thus, simultaneous reduction and nitrogen doping of GO is achieved by a one-step process. There is no significant difference

in Fe 2p spectrum after reduction with hydrazine, signifying that the chemical reduction was not detrimental to the Fe₃O₄ structure (Figure 3-13f). r[SPION/GO]₉ surface contains 72.4% C, 18.6% O, 5.9% N, and 3.1% Fe (at%). The increase in C and the decrease in O content after treatment with hydrazine is expected due to the deoxygenation of GO structure and restoration of carbon-carbon bonds during reduction. N content increased from 1.7 to 5.9% which validates nitrogen doping during chemical reduction. Naturally, Fe has a higher percentage after reduction due to decrease in oxygen content of GO even though the amount of Fe remains the same in the structure.

3.2.3.2. EPR Characterization of SPION/GO Thin Films

EPR spectroscopy is not only able to detect, distinguish and characterize paramagnetically active transition metal ions such as Fe³⁺ (S=5/2, I=0) but also give detailed information about their local environment. Here we deal with two main issues via EPR spectroscopy: i) intrinsic defect states in graphene and ii) electronic state of Fe ions.

In Figure 3-14a EPR of GO and rGO was compared. In general, two EPR signals can be observed in carbonaceous samples: a broad signal at g~2.002 attributed to graphitic-like carbon, and a sharper signal also at g~2.002 associated with carbon free radicals. The relatively narrower line of GO in Figure 3-14a could be attributed to signal of carbon radicals. Such carbon related radicals indeed caused by conduction electrons and dangling bonds, with different EPR characteristics. Reducing GO heals all these defect centers and gives almost defect-free graphene structure. Since such defect centers can contribute positively to the electronic conductivity hence the electrochemical properties can be also enhanced. Consequently, we have considered here only GO for the composite structure with SPION due to its highly defective content. In comparison of SPION, [SPION/GO]₁, [SPION/GO]₃, and r[SPION/GO]₉ given in Figure 3-14b quite impressive EPR results were obtained. SPION revealed typical broad iron oxide EPR signal which is due to dipolar

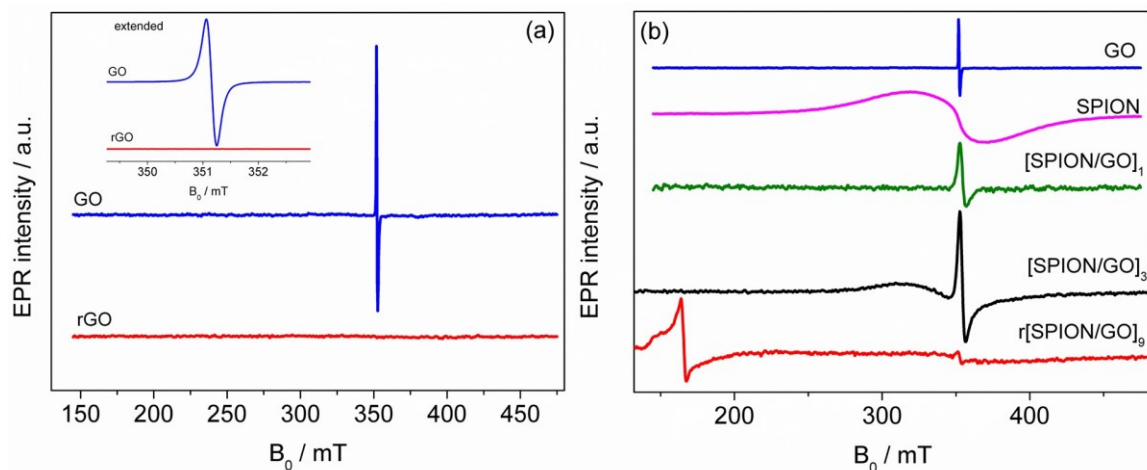


Figure 3-14 Comparison of room temperature X-band continuous wave EPR spectra of (a) GO and rGO (inset: enlargement of both spectra) (b) GO, SPION, [SPION/GO]₁, [SPION/GO]₃ and r[SPION/GO]₉. Note that, the intensity of [SPION/GO]₃ and r[SPION/GO]₉ is multiplied

interaction or commonly called spin-spin interactions. All Fe^{3+} spins interact with each other and reveals the broadening of EPR lines. In composite films [SPION/GO]₁ and [SPION/GO]₃ revealed plenty of carbonaceous related radicals. However, compared to GO signal it become broader indicating that SPION affected the carbon centers and caused their environment more anisotropic than in GO case. This is mainly due to existence of dangling bonds in graphene cages. [SPION/GO]₁ and [SPION/GO]₃ show somehow slightly different lineshape indicating that by changing the layer number the local environment is changing. From EPR results, one can say that the dangling bonds and the carbon radicals have much more concentrated at high number of layers with less symmetric neighborhood. Finally, r[SPION/GO]₉ sample gives very nicely isolated in other words diluted Fe^{3+} EPR spectra indicating that Fe^{3+} ions are incorporated in GO lattice with highly symmetric environment. Such Fe^{3+} incorporation in GO smeared out all dangling bond related defects and we only left with Fe^{3+} EPR spectra arising at lower fields with effective g -factor $g=4.23$. Similar Fe^{3+} spectra have been observed in our recent work on branched polyethyleneimine superparamagnetic iron oxide nanoparticles (bPEI-SPION).[143]

3.2.3.3. Electrochemical characterization of SPION/GO thin films

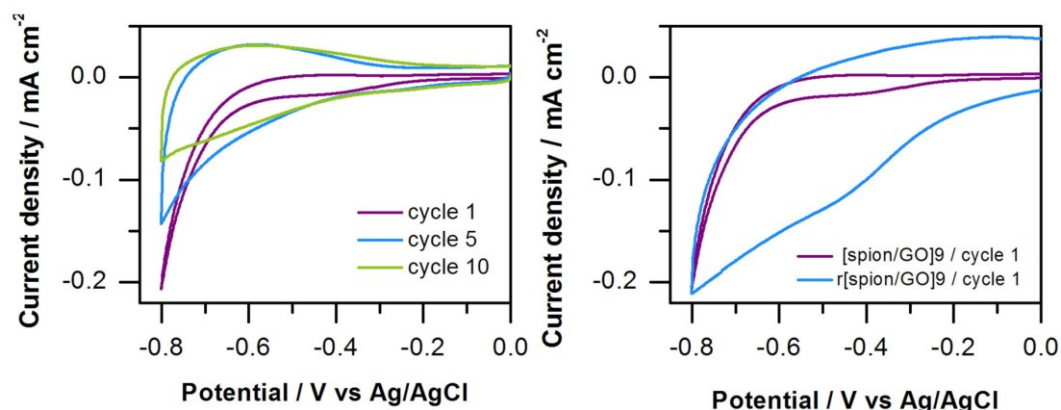


Figure 3-15 Cyclic voltammograms of 1st cycle of [SPION/GO]₉ and r[SPION/GO]₉ (b) 1st 10 cycles of [SPION/GO]₉

As mentioned before, SPION/GO films are transparent in their as-produced form. However, during the initial cycles of CV measurements, the color of the films turned immediately to dark gray, similar with the films treated with hydrazine (see Figure 3-9a), hence suggesting some degree of reduction during the CV process. In the first cycle of cyclic voltammogram of [SPION/GO]₉ film, a sharp tail is observed accompanied by a small capacitive current (Figure 3-15a). As the cycle number increases, the sharp tail vanishes and the shape of the voltammogram transforms into a symmetrical curve with increasing currents toward negative potentials (Figure 3-15a). Wang et al. [111] reported similar electrochemical reduction of GO onto ITO substrates in neutral electrolyte during CV measurement. They reported that the reduction peak appeared around -0.87 V (vs Ag/AgCl) and the onset potential of the peak extended towards -0.6 V, which is sufficient to initiate the reduction in our case. Similarity of the voltammogram of the as-prepared film after 10th cycle to the voltammogram of the hydrazine-reduced film in the first cycle proves that as-prepared films are reduced electrochemically to some extent during CV (Figure 3-15b).

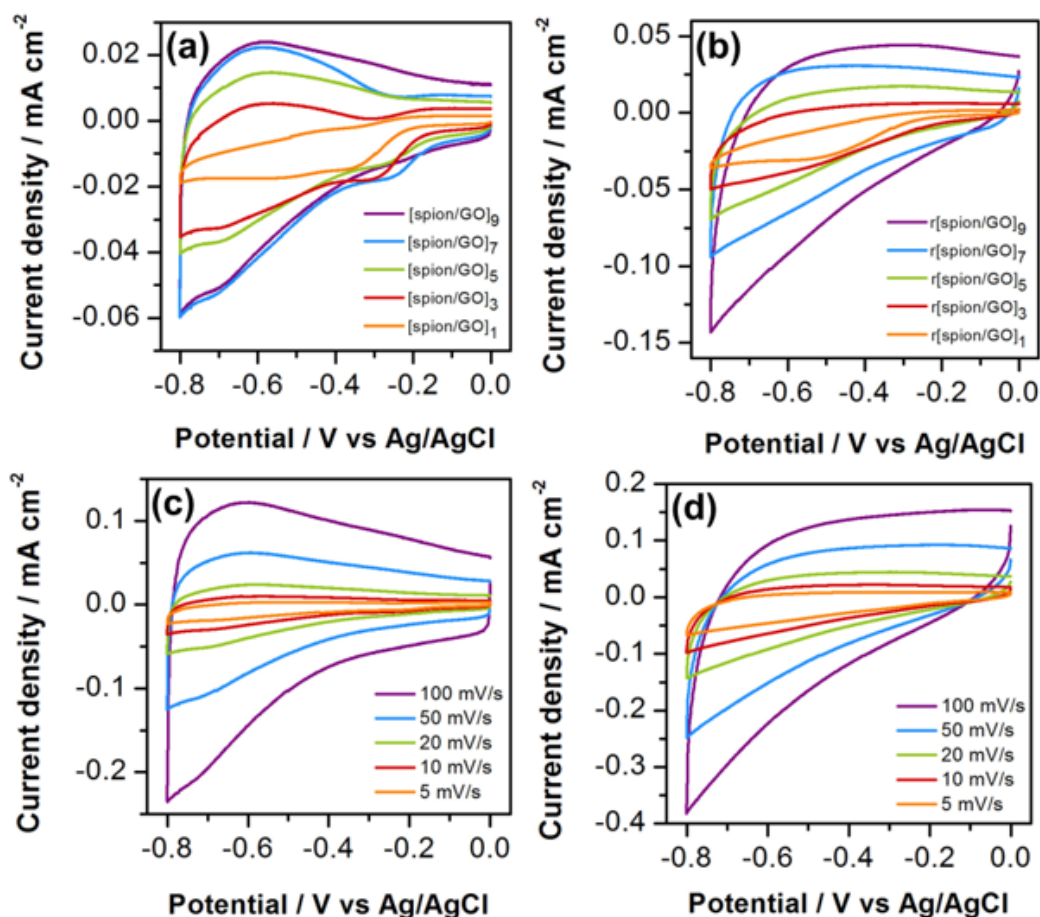


Figure 3-16 Cyclic voltammograms of (a) [SPION/GO] (b) r[SPION/GO] for different layers at 20 mV s^{-1} , (c) [SPION/GO]₉ (d) r[SPION/GO]₉ at different scan rates

Figure 3-16a shows voltammograms of as-produced films of bilayer numbers from 1 to 9. The current densities and the area enclosed by the curves increased with the number of bilayers, as expected. Additionally, two set of symmetrical peaks is observed around -0.3 and -0.7 V which are assigned to redox peaks of remaining functional groups of GO after mild electrochemical reduction. These peaks are more pronounced in 3, 5, and 7 bilayers and become indistinguishable with 9 bilayers. To further understand the origin of this redox peaks, hydrazine-reduced films' voltammograms are analyzed. (Figure 3-16b). The shape of the CV curves of r[SPION/GO] films is slightly tilted towards the negative potentials and resembles iron oxide voltammograms reported in the literature.[144] In this potential range (-0.8 – 0.0 V), only redox reactions between Fe^{2+} and Fe^{3+} is observed and no distinguished peaks are visible. The absence of the peaks at -0.3 and -0.7

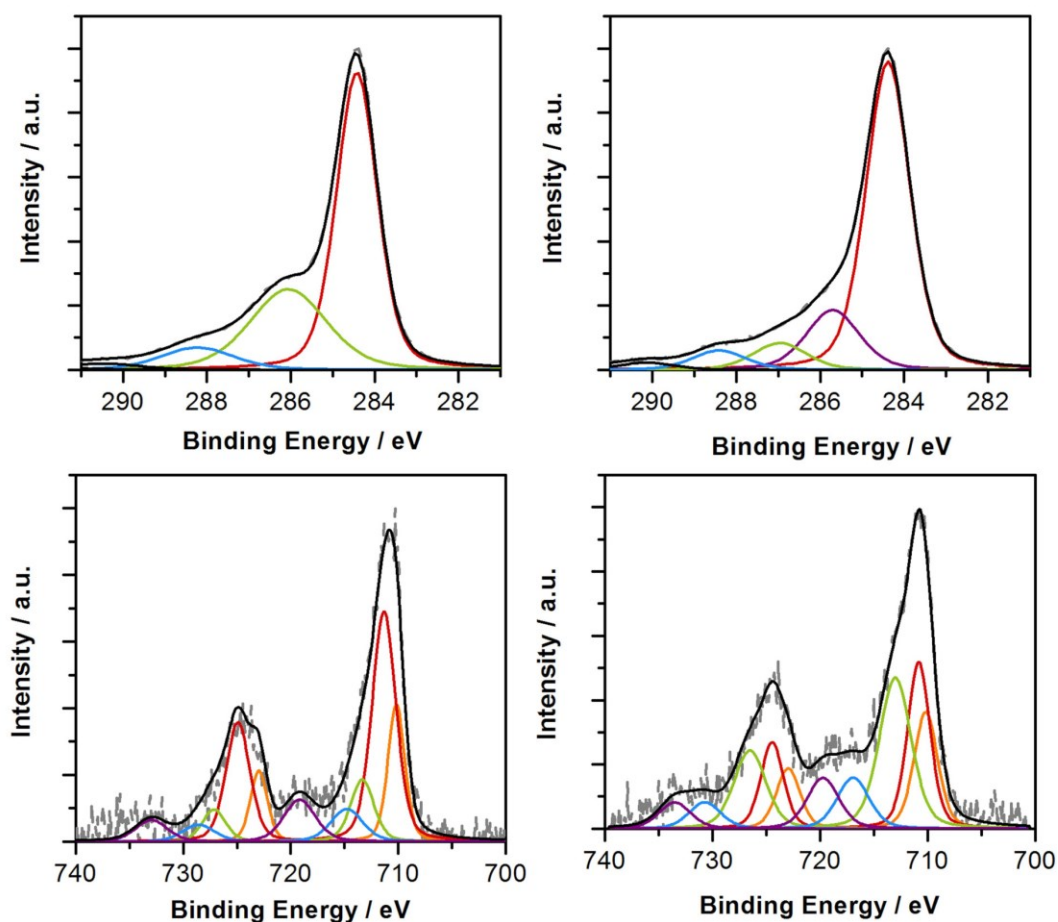


Figure 3-17 XPS C1s spectrum of (a) [SPION/GO]₉, (b) r[SPION/GO]₉, Fe2p spectrum of (c) [SPION/GO]₉, (d) r[SPION/GO]₉. All spectra were recorded after 10000 cycles of CV measurement

V vs Ag/AgCl in the voltammograms of r[SPION/GO] validates that the redox peaks in as-produced films originate from oxygen functional groups in GO.

Table 3-1 Relative intensities of functional groups normalized to C-C peak intensity calculated from XPS C1s spectra

Sample	C-N	C-O	C=O
[SPION/GO] ₉	x	0.93	0.12
[SPION/GO] ₉ _after cyclic stability	x	0.27	0.07
r[SPION/GO] ₉	0.23	0.07	0.06
r[SPION/GO] ₉ _after cyclic stability	0.19	0.09	0.06

When the XPS C1s spectrum of [SPION/GO]₉ after cyclic stability testing (shown in Figure 3-17a) is analyzed, a significant decrease in relative intensities C-O (0.27) and C=O (0.07), compared to that of pristine film. However, the relative intensities of functional groups are still higher than the values of hydrazine-reduced film (see Table 3-1). Thus, electrochemical reduction really occurred during the CV measurement, but it is less effective than hydrazine reduction since the amount of the functional groups were still present in higher amount after a longer duration (44 hours of CV compared to 10 h of hydrazine reduction). Consequently, as produced films' electrical conductivity should be lower than that of hydrazine-reduced films due to higher oxygen content: the lower conductivity is reflected in the areal capacitance values of as-produced films (Figure 3-18a). At scan rate of 20 mV s⁻¹, [SPION/GO] had areal capacitance of 0.39, 0.54, 0.72, 1.00, and 1.06 mF cm⁻² for bilayers of 1, 3, 5, 7, and 9, respectively. These values increased almost 2-fold after reduction and reached 0.65, 0.76, 1.05, 1.70, and 2.39 mF cm⁻² for the corresponding bilayers (Figure 3-18b). At higher scan rates (>20 mV s⁻¹), the capacitance values increase with increasing number of layers but at the lower ones, the trend is no longer observed. Nonetheless, areal capacitance values decreased with increasing scan rates for all the films, which is expected due to the imbalance between ion diffusion and charge-discharge rate. [36] The specific capacitance values for as-produced films are calculated by dividing areal capacitance values to the mass values calculated using QCM measurements (Figure 3-18c). At 5 mV s⁻¹, as-produced films had specific capacitances of 845, 337, 144, 154, and 100 F g⁻¹ for bilayers from 1 to 9. These values are retained as 99, 95, 82, 87, and 74 F g⁻¹ at 100 mV s⁻¹ for the corresponding bilayers. Hydrazine reduction of SPION/GO films boosted the SC values: 1569, 479, 266, 242, and 304 F g⁻¹ at 5 mV s⁻¹ for reduced bilayers of 1 to 9, respectively (Figure 3-18d). At 100 mV s⁻¹, SCs of 145, 109, 95, 116, and 106 F g⁻¹ were obtained for 1 to 9 bilayers. The specific capacitance of r[SPION/GO]₁ film at 5 mV s⁻¹ is almost ten-fold higher than the values reported in the literature for LBL assembled magnetite coupled with graphene or CNT films. [135,145] The reason for the extraordinary performance of the 1 bilayer film may be the maximum utilization of iron oxide nanoparticles and surface of the

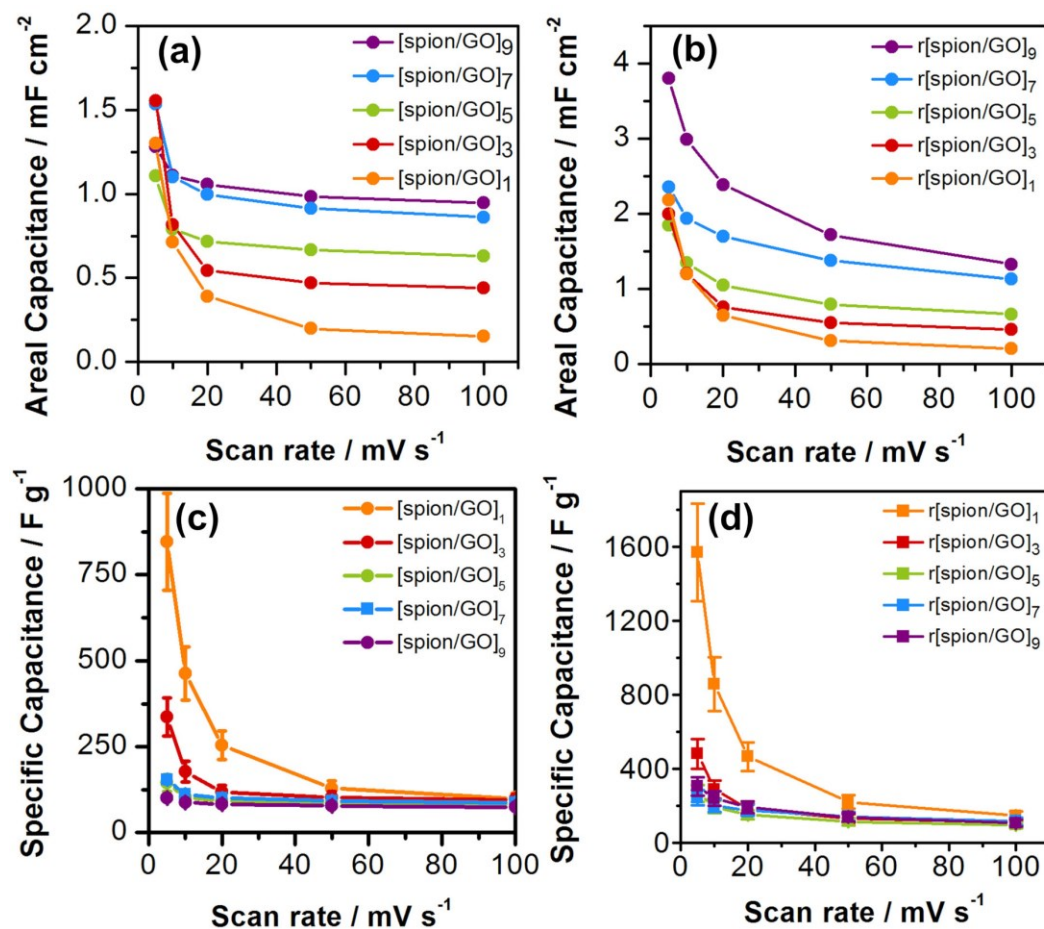


Figure 3-18 Areal capacitance values of (a) [SPION/GO] (b) r[SPION/GO], specific capacitance values of (c) [SPION/GO] (d) r[SPION/GO] from bilayers 1 to 9 at different scan rates (error bars represent the SC change within standard deviation)

graphene because overall structure is exposed to the electrolyte directly and the electrons/ions pass easily pass within the layers towards the current collector. With increasing number of layers, exploitation of capacitance of the layers close to ITO decreases and is limited by the diffusion between top and the bottom layers. Consequently, the specific capacitance values decreased with increasing number of bilayers at the same scan rate (Figure 3-18c,d). Nevertheless, higher bilayers also exhibited superior performance compared to other magnetite-graphene composites produced with LBL method. r[SPION/GO]₅ film has almost three-fold specific capacitance value at 5 mV s⁻¹ than hydrazine-reduced magnetite-rGO composite. [134] Moreover, r[SPION/GO]₉ film specific capacitance at 5 mV s⁻¹ is almost four-fold higher than magnetite-FLG, even though it was reported at a lower scan rate. [135] The superior performance of our SPION/GO films may be

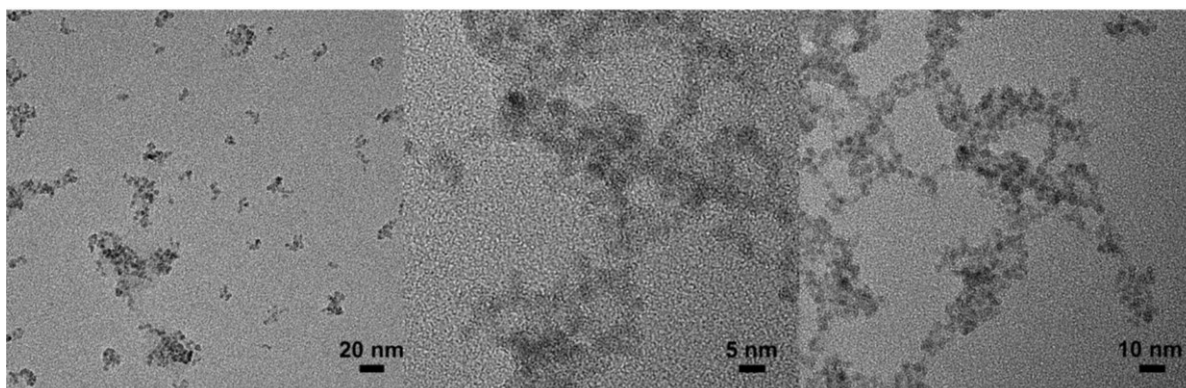


Figure 3-19 TEM images of APTMS coated SPION

resulting from several factors. The high dispersion of iron oxide nanoparticles (average crystal size about 5 nm and hydrodynamic size of 10-20 nm, see Figure 3-19 and Figure 3-20b for TEM and DLS analysis) on GO layers facilitates redox reactions of iron oxide and functional groups of GO. From the EPR results, it was observed that $r[\text{SPION}/\text{GO}]_9$ had nicely isolated Fe^{3+} centers on the $r\text{GO}$ structure with a highly symmetric environment. Moreover, APTMS content of SPION (see Figure 3-20a for TGA of APTMS coated SPION) enhances interaction between iron oxide and GO via H-bonding and electrostatic interactions. All the aforementioned factors contribute to the overall superior performance of SPION/GO films.

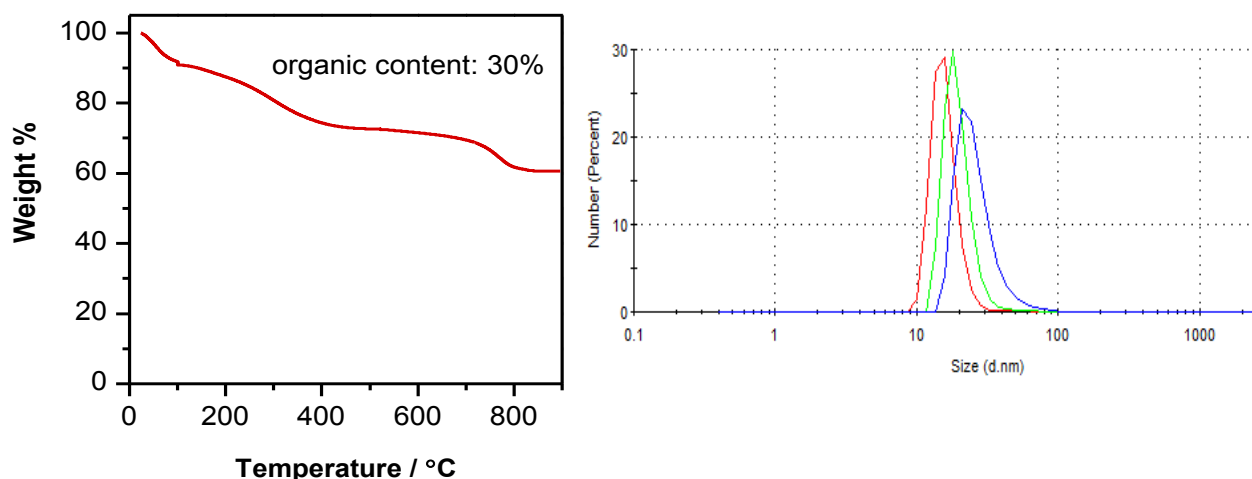


Figure 3-20 (a) TGA curve of APTMS coated SPION under N_2 at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ (b) Number average hydrodynamic size distribution of APTMS/SPION measured by DLS

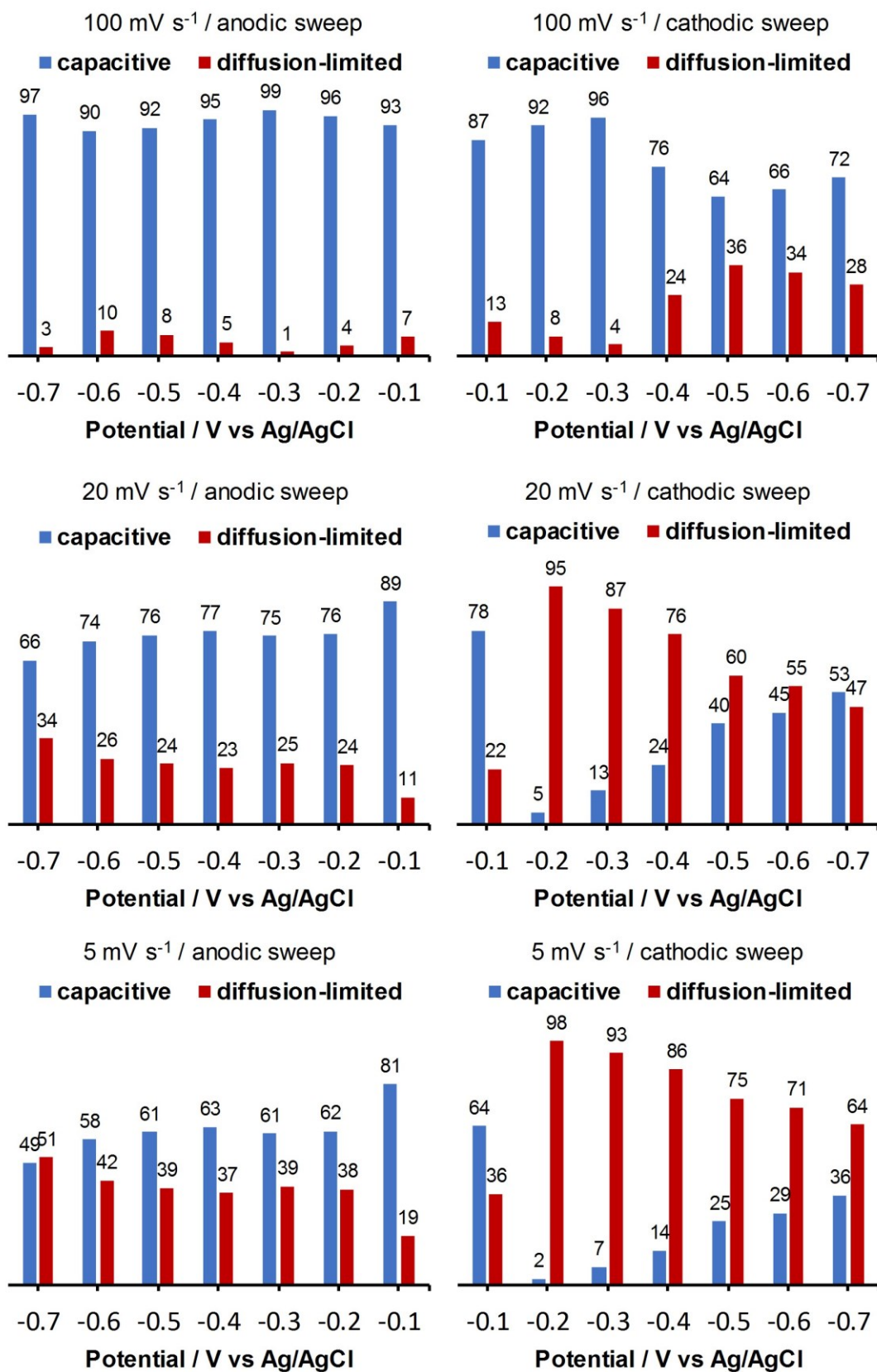


Figure 3-21 Charge storage mechanism analysis of [SPION/GO]₉

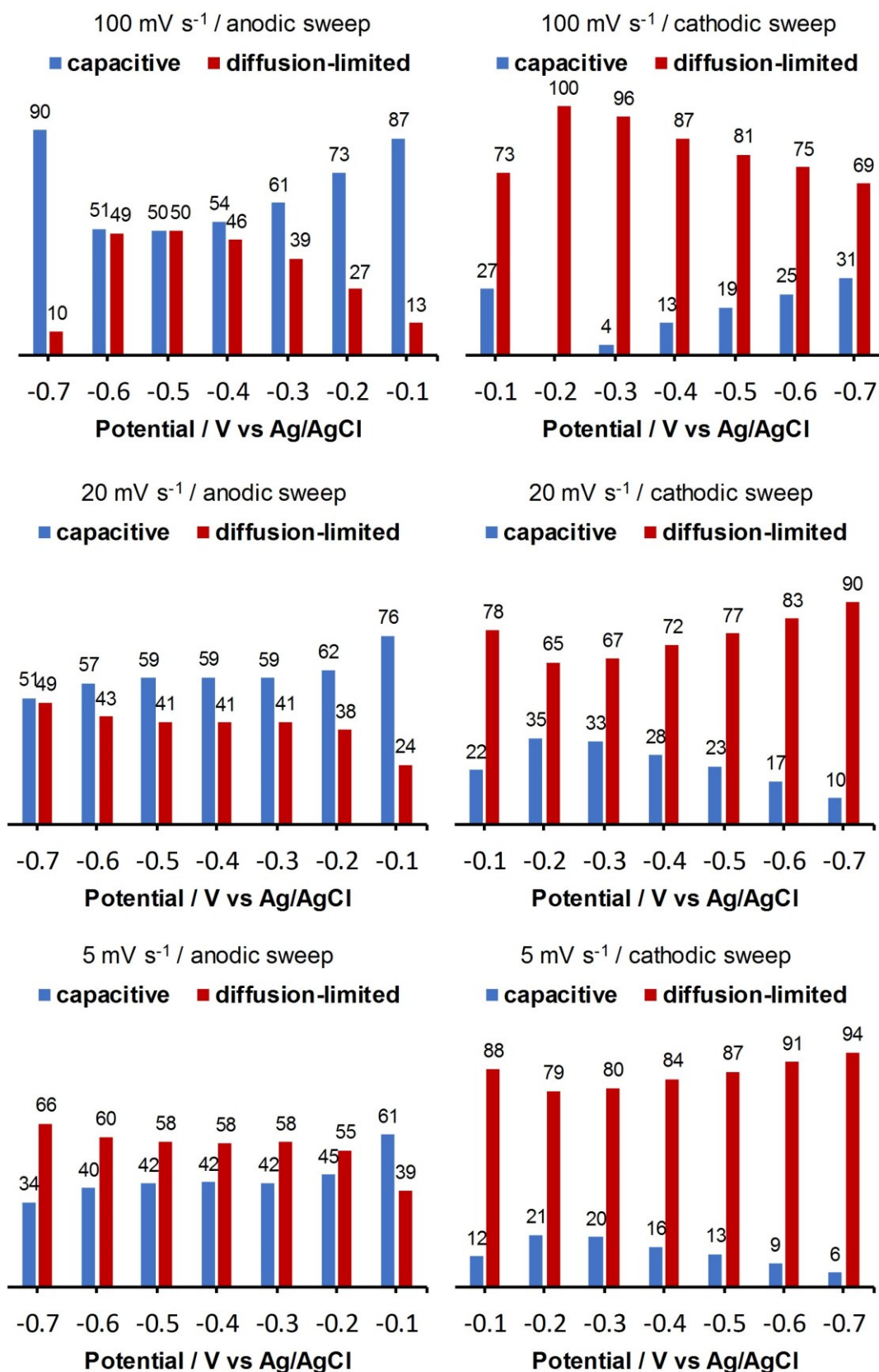


Figure 3-22 Charge storage mechanism analysis of r[SPION/GO]₉

To investigate the nature of charge storage mechanisms of as-deposited and reduced films, variations of current with sweep rate in CV measurements were calculated as explained in Section 2.3.3. Accordingly, the percentages of current arising from the capacitive and diffusion-limited processes are calculated and the values are given in Figure 3-21 and Figure 3-22.

For [SPION/GO]₉, almost all the capacitance comes from capacitive mechanism at higher scan rates. At lower scan rates, however, capacitive contribution decreases, especially in cathodic sweep. In comparison, r[SPION/GO]₉ exhibit diffusion-limited charge storage like batteries at all scan rates. The charge storage becomes almost fully diffusion-limited in cathodic sweep. This difference is reflected in cyclic stability measurements: hydrazine-reduced film has a constant decay in performance with increase in cycle numbers which is a typical behavior observed in batteries. Whereas as-produced film becomes stable after certain number of cycles (around 2000) and preserves almost 95 % of the capacitance value at 10000 cycles (Figure 3-24). The decrease until 2000 cycles may be caused from the, incomplete reduction of as-produced film. As previously mentioned, as-produced films undergo electrochemical reduction during initial cycles of CV. However, the reduction may be proceeding slowly since the lower potential limit of CV (-0.8 V vs Ag/AgCl) is more positive than the peak potential of GO/rGO reduction reported in the literature (-0.87 V vs Ag/AgCl). [111] It is very well-known that GO exhibits superior electrochemical performance than graphene due to pseudocapacitive properties arising from oxygen functional

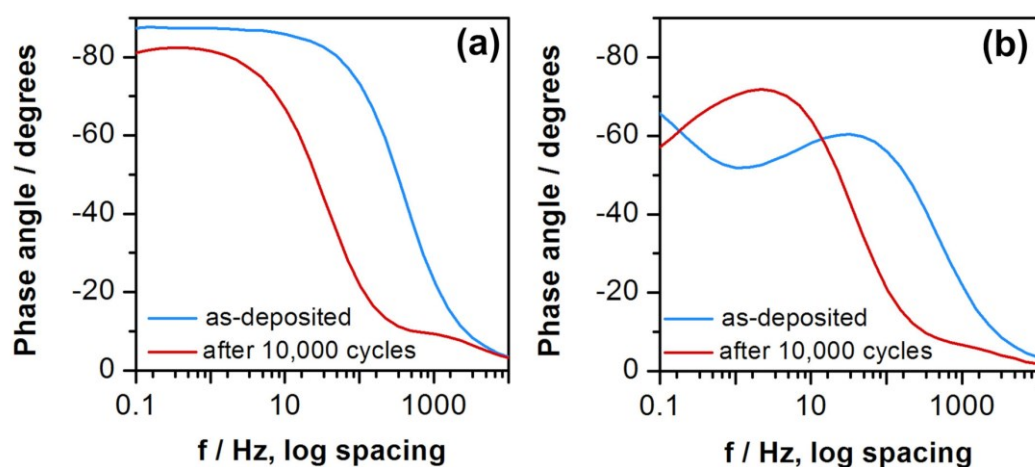


Figure 3-23 Bode plots of (a) [SPION/GO]₉ and (b) r[SPION/GO]₉ before and after cyclic stability test

groups, although it has lower electrical conductivity and specific surface area. [47] Thus, the capacitance may be decreasing during CV, and reaching maximum reduction degree around 2000 cycles.

Bode plots shown in Figure 3-23 enables us to calculate relaxation time constants, τ_0 , which is the point where resistance and reactance of capacitance are equal [146], and also interpreted as the minimum time required to dissipate all the energy from the system with an efficiency higher than 50%. [147] The relaxation time constants are calculated from conversion of frequencies at the phase angle of -45° ($\tau=1/f$). [SPION/GO]₉ has τ_0 of 2.57 ms which is much shorter than activated carbon and carbon onion microsupercapacitors. [132] The relaxation time increased to 31.6 ms after 10000 cycles of CV measurement (Figure 3-23) which is reasonable since a transformation occurred in the structure due to electrochemical reduction, and the defects produced during this process may be responsible for the increased time constant. [75]

Nevertheless, at lower frequencies, the maximum phase is -87.4° , almost close to -90° which is typically observed in ideal capacitors. [148] The maximum phase angle decreases to -81.1° after 10000 cycles (Figure 3-23a), still a reasonably close value to -90° . Figure 3-23b shows the Bode plots for r[SPION/GO]₉ before and after cyclic stability tests. Before the stability test, the phase angle approaches -65.7° with a maximum appearing around -60.4° which indicates a diffusion-induced resistance. After the stability test, the maximum shifts to lower frequencies revealing increase in the resistance. [149] The decay in diffusion is also reflected in lowered maximum phase angle after stability test (-57.1°). Additionally, relaxation time constants are higher than that of as-produced films. Thus, hydrazine-reduced films exhibited high electrochemical performance originating from mainly diffusion-limited charge storage characteristics, deviating from ideal capacitive behavior. Although these films probably have higher electrical conductivity (indicated by higher C/O ratio and larger areal/specific capacitance), the harsh reducing nature of hydrazine

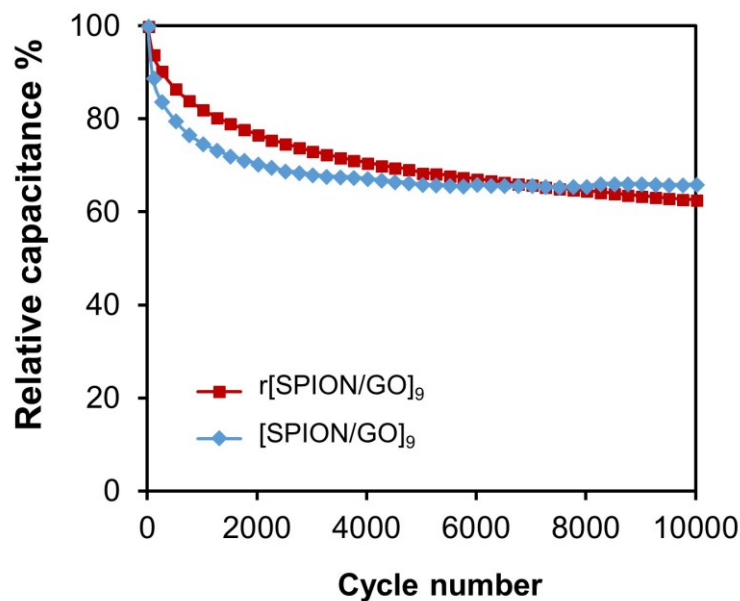


Figure 3-24 Cyclic stability curves of [SPION/GO]₉ and r[SPION/GO]₉

vapor may have been detrimental to the synergistic interaction between graphene and iron oxide nanoparticles. Also, SPION-GO interaction may have been weakened due to lower amount of the oxygen functional groups and the defect centers in rGO compared to that of GO (as shown with XPS and EPR) resulting in decreased cyclic stability.

3.2.4. Conclusions

In this section, ultrathin supercapacitor electrodes consisting of APTMS coated SPION and GO layers were produced with a simple and low-cost dip coating technique. The effect of increasing number of bilayers and the chemical reduction on the electrochemical performance was investigated. The areal capacitance of as-deposited films was tuned between 0.39 and 1.06 mF cm⁻² at 20 mV s⁻¹ by simply increasing the bilayer from 1 to 9, respectively. These values were almost doubled after chemical reduction with hydrazine vapor due to restoration of defect-free graphene structure and increase in electrical conductivity. EPR results showed the effect of competing between carbon related defects and Fe related paramagnetic centers. As a result of the highly symmetric Fe³⁺ centers in GO layers, r[SPION/GO]₉ electrode exhibited extraordinary specific capacitance of 1570 F g⁻¹ at 5 mV s⁻¹. This value is ten-fold higher than that of LBL assembled iron

oxide nanoparticles coupled with CNT/graphene reported in the literature. The analysis on the charge storage mechanism revealed that the as-deposited films had pseudocapacitive properties, whereas hydrazine reduced films were controlled with diffusion-limited processes. In fact, as-deposited films showed higher cyclic stability than the chemically reduced counterparts.



Chapter 4: Graphene Aerogels

4.1. Introduction

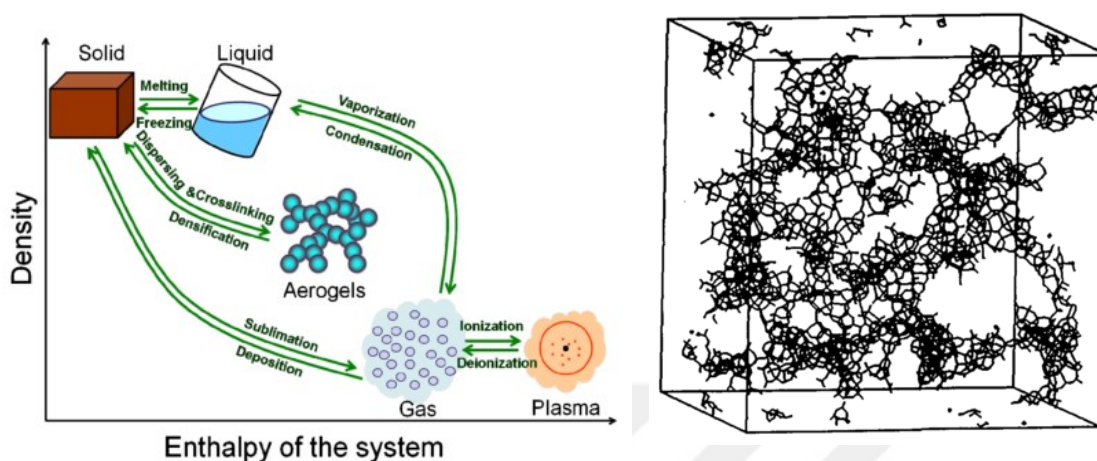


Figure 4-1 Density vs enthalpy diagram for different states of matter (left), schematic representation of an aerogel network (right) [151,154]

Aerogel is defined as “gel comprised of a microporous solid in which the dispersed phase is gas” by IUPAC. [150] In other words, aerogels are highly porous gels derived from the replacement of dispersing liquid (solvent) with a gas (air). There are several classes of aerogels used in the literature, classified by their composing material: silica, resorcinol formaldehyde (RF), chalcogenide, carbon nanotube (CNT), carbon, metal-oxide, and graphene aerogels are the commonly studied examples. [151–153] In general, aerogels are low-density materials ($0.004 - 0.500 \text{ g cm}^{-3}$) with well-accessible branched mesopores which results in high specific surface area (Figure 4-1). [154] For comparison, air has density of $0.00129 \text{ g cm}^{-3}$ indicating aerogels can be as "light" as air. A gel is composed of solid particles crosslinked to each other which are dispersed in a liquid. The gel is named as hydrogel or alcogel depending on the solvent (water or alcohol). To produce an aerogel from a hydr(alc)ogel, special drying techniques must be employed since ambient drying can induce collapse of the porous structure. The collapse can be resulted from two reasons: first, slower drying of the interior of the gel produces pressure gradient causing cracks. Second, imbalanced drying of differently-sized pores uneven stress since larger pores empty faster than the smaller ones. [154] Overall, ambient drying causes shrinkage of the gel network, mainly due to capillary forces acting

on the small pores. As a result, “xerogel” is formed when a wet gel is dried conventionally (Figure 4-2). To produce aerogels from the wet gel, special drying methods must be utilized as stated before. Three commonly utilized methods to dry wet gels include: freeze-drying, drying in organic solvents (hot), and supercritical CO₂ drying (cold). [155] Freeze-drying is applied by rapidly freezing the wet gel (solvent) followed by sublimation of the solid via subjection to high vacuum.

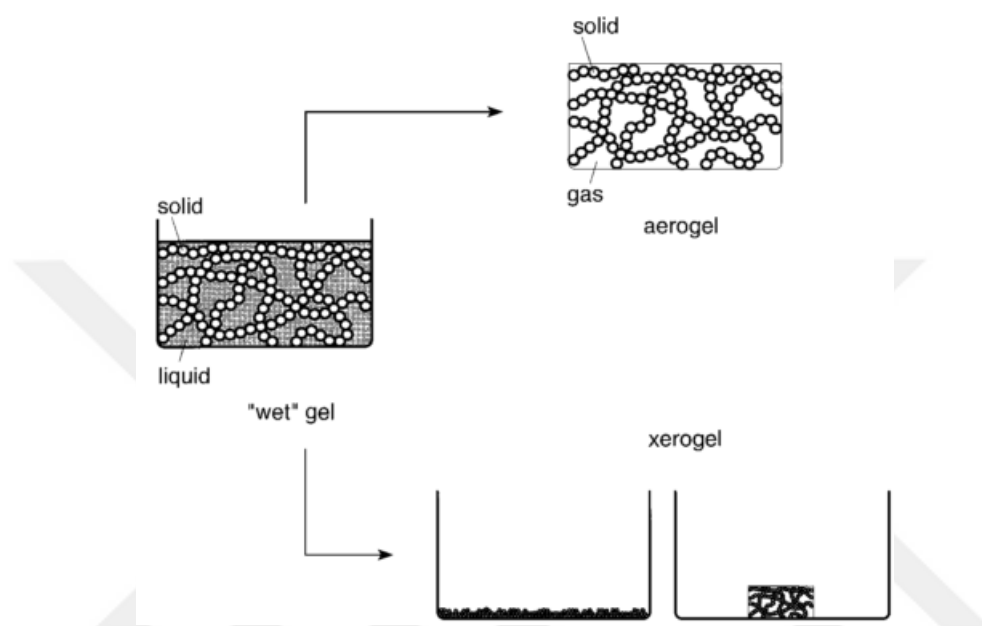


Figure 4-2 Formation of aerogel and xerogel upon different drying conditions [154]

Although the technique is simple and low-cost, the formation of ice crystals is detrimental to the pore structure due to expansion of volume during water to ice transition. Other two techniques utilize supercritical fluids for drying. Supercritical fluids formed when the temperature and pressure exceed the critical point in the phase diagram of a material. [156] Supercritical fluids have liquid-like densities and gas-like viscosities. The critical pressures and temperatures of commonly used fluids are shown in Figure 4-3. Alcohols have critical temperatures around 250 °C and pressures of 5-10 MPa. One of the methods to dry wet-gels, drying in organic solvents include use of supercritical organic solvents, which requires high temperatures (>250 °C). Apart from the high-flammability of organic solvents, use of high temperatures is also detrimental to the porous structure of the gels. [154] In this regard, use of supercritical CO₂ for drying seems to be the ideal choice for producing aerogels. CO₂ is a non-toxic, inexpensive, non-flammable, and inert gas

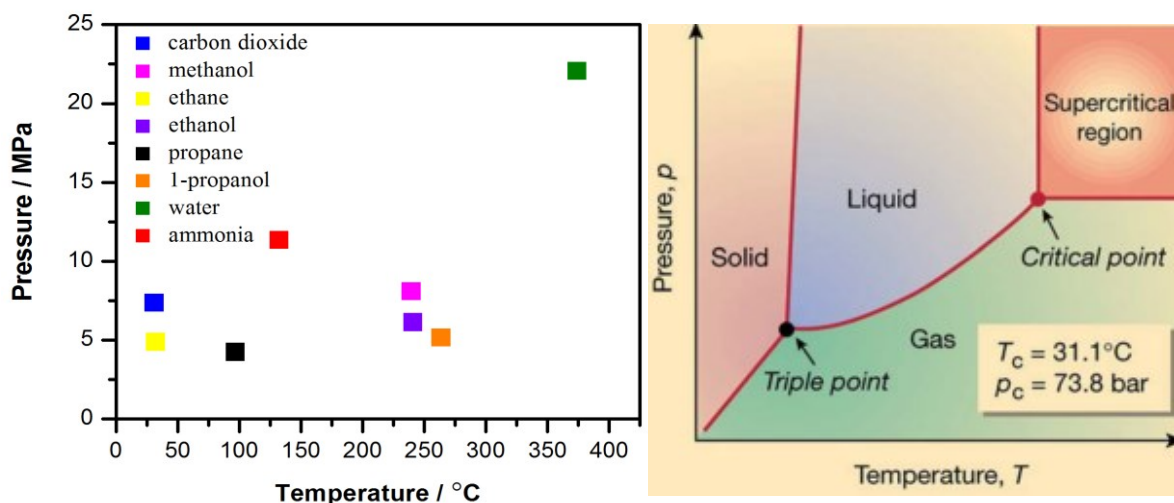


Figure 4-3 Critical temperatures and pressures of some fluids (left) Phase diagram of carbon dioxide (right) [156]

which is produced as a by-product from many industrial plants. It has also moderate critical temperature and pressure (31.1 °C, 7.4 MPa) compared to other fluids (Figure 4-3). Since supercritical CO₂ (scCO₂) has zero surface tension, it facilitates drying of gels without structural deformation.

Graphene aerogels (GAs) are aerogels composed of randomly stacked graphene sheets. These materials bring together the aforementioned characteristics of aerogels with that of graphene. Since the first report published in 2010 by Xu. *et al.* [157], hydrothermal self-assembly is one the most studied technique in the literature to produce GAs. Hydrothermal synthesis of GA includes heating of GO solutions dispersed in water (or any other solvent) in a closed vessel until a monolithic structure is obtained. During the hydrothermal reaction, simultaneous reduction of GO sheets takes place due to applied heat and pressure. Upon reduction, the hydrophobic interaction and π - π^* stacking between restored graphene sheets is believed to drive the formation of hydrogel structures. [158] Hu et al. investigated the driving forces for the hydrothermal self-assembly of GO sheets in detail with potentiometric titrimetry and thermogravimetric analysis. [159] The formation of porous network resulted from entrapping of CO₂ between partially reduced GO layers. During the hydrothermal reaction, possible mechanisms to evolve CO₂ are investigated as shown in Figure 4-4. Route 1 is the decarboxylation of carboxylic acids favored by high

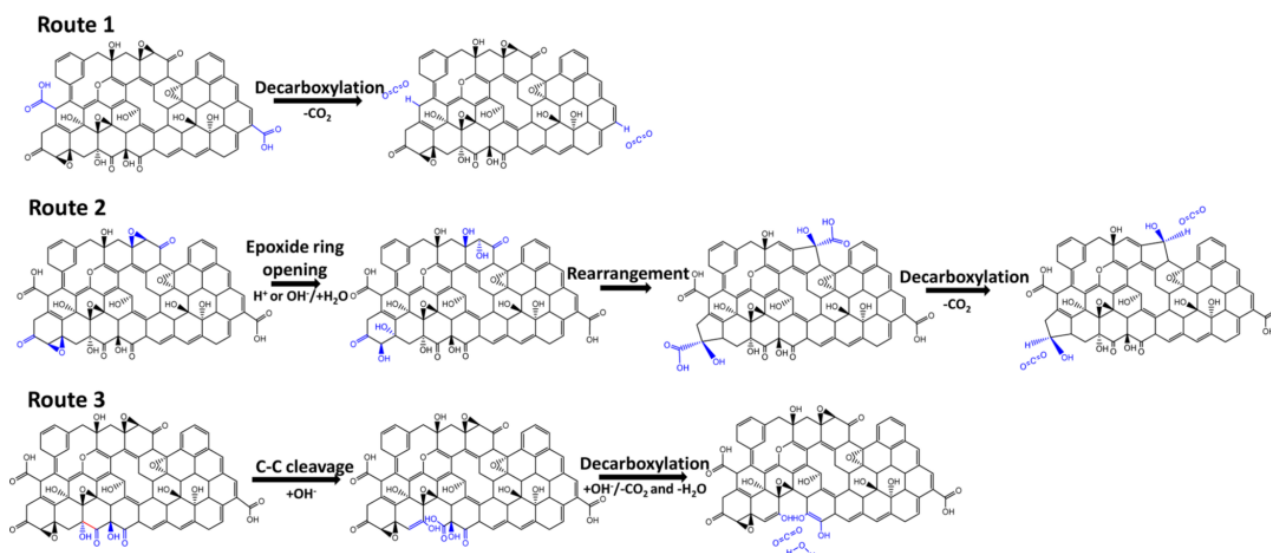


Figure 4-4 Possible reaction pathways occurring during hydrothermal reaction of GO to produce CO₂ [159]

temperatures (>70 °C). Route 2 is the acid/base catalyzed ring opening of epoxides followed by the rearrangement of diols and ketones formed to produce new carboxylic acids; these later decompose to form CO₂. Route 3 is the cleavage of C-C bond between carbons bearing hydroxyl and carbonyl groups, and formation of new carboxylic group and C=C bond which later form CO₂ with nucleophilic attack of water. This study also mentions high mechanical strength of GA formed from acidic GO solutions due to formation of more compact structure.

For electrochemical applications, especially ECs, GAs are ideal materials with combined high mechanical strength, specific surface area, and electrical conductivity. Cheng et al. [160] reported enhanced mechanical and thermal properties of GA dried with supercritical ethanol at 270 °C and 8 MPa. The highest BET surface area ($602.8 \text{ m}^2 \text{ g}^{-1}$) was obtained for GA synthesized from initial GO concentration of 2.0 mg mL^{-1} . Jung et al. [161] studied the effect of pore structure on the electrochemical properties. They prepared GAs with three different freeze-drying temperatures (-20, -80- and -200 °C). The corresponding BET surface areas are 504, 441, and $315 \text{ m}^2 \text{ g}^{-1}$, respectively. The specific capacitances calculated at 1 A g^{-1} were 325, 230, and 125 F g^{-1} for the samples dried at -20, -80, and -200 °C, respectively. Consequently, increasing the surface area influenced the electrochemical performance in a positive way. Comparison of the effect of drying

technique on the electrochemical performance is investigated by Zhang et al. [162]. They performed scCO₂ or freeze-drying to obtain GAs followed by CV measurements in 6 M KOH. The BET surface area of freeze-dried and scCO₂ dried samples were 11.8 and 512 m² g⁻¹, respectively. scCO₂-dried GA exhibited specific capacitance of 128 F g⁻¹ at 0.05 A g⁻¹ while the performance of freeze-dried sample was not reported. All the GAs and their composites reported in the literature are summarized in Table 4-1 which includes surface area values and electrochemical performances (if available). Among these studies, surface areas obtained by freeze-drying are in the range of 200-300 m² g⁻¹ while surface areas as high as 800-900 m² g⁻¹ can be attained by scCO₂ drying.

This chapter includes synthesis of GA with one-step hydrothermal self-assembly of acidic GO solutions followed by scCO₂ drying. The structural characteristics of produced GA are investigated by XRD, Raman, TGA and XPS measurements. The pore structure of GA is analyzed by N₂ adsorption experiments. The electrochemical properties of GA are investigated by CV and RDE measurements.

Table 4-1 Electrochemical properties of graphene aerogels (composites) reported in the literature

Reference	Material	Synthesis/drying method	BET surface area / m ² g ⁻¹	Electrochemical performance	Electrolyte
[163]	N-GA	Hydrothermal (GO+NH ₃) / Freeze drying	NA	245 F g ⁻¹ at 0.1 A g ⁻¹	1 M H ₂ SO ₄
[164]	N-GA	Wet chemical (GO+melamine) / Freeze drying	723	150 F g ⁻¹ at 0.3 A g ⁻¹	PVA/KOH gel
[165]	GA	Hydrothermal (GO) / Freeze-drying	NA	237.1 F g ⁻¹ at 1 A g ⁻¹	6 M KOH

Reference	Material	Synthesis/drying method	BET surface area / m ² g ⁻¹	Electrochemical performance	Electrolyte
[166]	GA/N-GA	Hydrothermal (GO+NH ₃) / Freeze-drying	GA: 307.1 NGA:520.6	150 F g ⁻¹ at 1 A g ⁻¹	2 M KOH
[167]	N-GA	Hydrothermal (GO+urea) / Freeze-drying	GA: 307.1 NGA:520.6	153.8 F g ⁻¹ at 1 A g ⁻¹	2 M KOH
[168]	N-GA	Wet chemical (GO+EDA) / Freeze drying	NA	325 F g ⁻¹ at 0.5 A g ⁻¹	1 M KOH
[169]	N,S-3D rGO	Hydrothermal (GO+thiosemicarbazide) / Freeze-drying	NS-rGO: 228 rGO: NA	NS-rGO: 249.4 F g ⁻¹ at 1 A g ⁻¹ rGO: NA	3 M KOH
[170]	GA	Wet chemical (GO) / Freeze drying	NA	208 F g ⁻¹ at 2 A g ⁻¹	2 M KOH
[171]	GA	Hydrothermal (GO) / Freeze-drying	NA	124 F g ⁻¹ at 1 A g ⁻¹	0.5 M Na ₂ SO ₄
[172]	NGA	Wet chemical (GO+cellulose)/ Freeze drying	NA	322.7 F g ⁻¹ at 1 mV s ⁻¹	6 M KOH
[173]	GA	Hydrothermal (GO)/ Freeze-drying	168.6	286.9 F g ⁻¹ at 1 A g ⁻¹	2 M KOH
[174]	GA	Hydrothermal (GO) / Freeze-drying	NA	GA2: 305 F g ⁻¹ at 10 A g ⁻¹ GA1: 280 F g ⁻¹ at 10 A g ⁻¹	1 M H ₂ SO ₄
[175]	N-GA	Hydrothermal (GO+hydrazine) / Freeze-drying	NGA: 368.25	400 F g ⁻¹ at 25 mV s ⁻¹	1 M KOH

Reference	Material	Synthesis/drying method	BET surface area / m ² g ⁻¹	Electrochemical performance	Electrolyte
[176]	GA	Hydrothermal (GO) / Freeze-drying	185	12.5 mF cm ⁻¹ = 62.3 F g ⁻¹	
[177]	N-GA	Hydrothermal (GO+hydrazine) / Freeze-drying	NA	392 F g ⁻¹ at 0.5 A g ⁻¹	0.2 M PBS
[178]	GA	Hydrothermal (GO+F127) / Freeze-drying	173	198 F g ⁻¹ at 0.1 A g ⁻¹	
[179]	N-GA	Hydrothermal (GO+hydrazine) / Freeze-drying	294	320 F g ⁻¹ at 10 mV s ⁻¹	Na ₂ SO ₄
[180]	GA	Freeze-drying from graphene ink	GA: 400	123 F g ⁻¹ at 1 A g ⁻¹	1 M H ₂ SO ₄
[181]	GA	Wet chemical (GO+L-ascorbic acid) / Freeze drying	29.3 to 41.2 depending on concentration	338.5 F g ⁻¹ at 2.5 A g ⁻¹	6 M KOH
[182]	3D printed GA	3D printing of GO+RF, scCO ₂ drying	436	57 F g ⁻¹ at 0.5 A g ⁻¹	PVA/LiOH gel
[183]	S,P-GA	Wet chemical (GO+thioglycolic acid+phytic acid+iodine+HP) /Freeze drying	GA: 305 S,P-GA: 409	GA: 240 F g ⁻¹ S,P-GA: 438 F g ⁻¹ at 10 mV s ⁻¹	1 M H ₂ SO ₄

Reference	Material	Synthesis/drying method	BET surface area / m ² g ⁻¹	Electrochemical performance	Electrolyte
[184]	GA	Solvothermal (GO) / Freeze-drying	HGA: 528 (Ar bubbled) GA: 305 (O ₂ bubbled)	HGA: 178 F g ⁻¹ at 0.2 A g ⁻¹ GA: 151 F g ⁻¹ at 0.2 A g ⁻¹	6 M KOH
[185]	GA	Hydrothermal (GO) / Freeze-drying	220	99 F g ⁻¹ at 5 mV s ⁻¹	6 M KOH
[186]	GA	Hydrothermal (GO) / Freeze-drying	NA	123.6 F g ⁻¹ at 5 mV s ⁻¹	1 M Na ₂ SO ₄
[187]	GA	Hydrothermal (GO) / Freeze-drying	220	130 F g ⁻¹ at 5 mV s ⁻¹	6 M KOH
[188]	N-GA	Hydrothermal (GO+NH ₃) / Freeze-drying	NGA: 830 GA: 710	NGA: 223 F g ⁻¹ at 0.2 A g ⁻¹ GA: 205 F g ⁻¹ at 0.2 A g ⁻¹	1 M H ₂ SO ₄
[161]	GA	Slow evaporation of graphene suspensions/freeze drying at different temperatures	T _f (-20 °C): 504 T _f (-80 °C): 441 T _f (-200 °C): 315	325 F g ⁻¹ at 1 A g ⁻¹	0.5 M H ₂ SO ₄
[189]	GA	Hydrothermal (GO) / Freeze-drying	NA	118 F g ⁻¹ at 1 A g ⁻¹	6 M KOH
[190]	Carbon/GA	Hydrothermal (GO+RF)/ Freeze-drying	GCA:891.2	116.6 F g ⁻¹ at 0.5 A g ⁻¹	6 M KOH

Reference	Material	Synthesis/drying method	BET surface area / m ² g ⁻¹	Electrochemical performance	Electrolyte
[191]	S-GA	Wet chemical (GO+thioglycolic acid+iodine+HP) /Freeze drying	S-GA: 359.5 GA: 276.5	S-GA: 445.6 F g ⁻¹ at 5 mV s ⁻¹ GA: 118.3 F g ⁻¹ at 5 mV s ⁻¹	1 M H ₂ SO ₄
[192]	GA	Solvothermal (GO in different solvents) / Freeze drying	IPA: 621 EtOH: 406 EG: 347	IPA: 287 F g ⁻¹ EtOH: 261 F g ⁻¹ EG: 244 F g ⁻¹ at 0.1 A g ⁻¹	6 M KOH
[193]	Porous carbon/GA	Hydrothermal (GO+porous carbon)/ Freeze-drying	Porous C/GA: 1221	porous C/GA: 410.8 F g ⁻¹ at 0.1 A g ⁻¹	6 M KOH
[194]	GA/carbon	Wet chemical (GO+RF)/ scCO ₂ drying	GA+carbon: 793	GA: 25 F g ⁻¹ at 25 mV s ⁻¹	0.5 M Na ₂ SO ₄
[195]	GA	Wet-chemical (GO) /scCO ₂ drying	GA: 866 rGA: 867	GA: 155 F g ⁻¹ at 0.1 A g ⁻¹ rGA: 90 F g ⁻¹ at 0.1 A g ⁻¹	30 wt% KOH
[196]	GA	Freeze drying GO onto nickel foam	GA: 463	366 F g ⁻¹ at 2 A g ⁻¹	6 M KOH
[157]	GA	Hydrothermal (GO)/freeze-drying	NA	175 F g ⁻¹ at 10 mV s ⁻¹	5 M KOH

4.2. Materials & Methods

4.2.1. Materials

All the chemicals were used as received without further purification. Graphite (natural, -200 mesh, 99.9995 %), K₂SO₄ (99%), and NaNO₃ (99 %) were obtained from Alfa Aesar. KMnO₄, ethanol

(EMPROVE), and H_2O_2 (30 %) were purchased from Merck Millipore. H_2SO_4 (95-97 %) and HCl (37 %) were obtained from Sigma Aldrich. Saturated calomel electrode (SCE, in saturated KCl) was purchased from Radiometer Analytical SAS, France. Reversible hydrogen electrode (RHE) was obtained from Gaskatel GmbH, Germany.

4.2.2. Synthesis of GA

Precursor GO solution was obtained via experimental route explained in Section 2.2.2.

GA was synthesized from GO solution via one-step hydrothermal route. 3.0 g L^{-1} GO solution was placed in a Teflon-lined stainless-steel autoclave and placed into a drying oven at 180°C for 3 hours. After cooling down to room temperature naturally, the vessel was opened, and the monolithic black hydrogel was placed into distilled water for 24 hours for purification. After exchanging water with acetone, the hydrogel was dried via supercritical CO_2 (Spe-ed SFE-15,000, Applied Separations, Inc.) at 50°C and 12.0 MPa; this process resulted in formation of a GA monolith.

4.2.3. Structural Characterization of GA

Crystal structure of GA was analyzed via XRD (Bruker D8 Advance) with $\text{Cu K}\alpha$ source. One spatula tip of GA powder was put onto low-background Si holder for the measurement. Morphological analysis was conducted with FESEM (Zeiss Ultra Plus). For FESEM measurement, GA monolith was carefully placed on the stub without pressing to observe porous structure. Defect analysis of GA was done with Raman (Renishaw Invia) with 532 nm laser. Laser power was set to 5 mW to avoid local heating. Fitting of Raman spectrum was done with Fityk software. Pore properties of GA was investigated by N_2 physisorption using surface area and porosimetry analyzer (Micromeritics ASAP 2020). Pore size distributions were determined by Barret, Joyner, and Halenda (BJH) method. Thermogravimetric analysis (TGA, TA Instruments TGA Q500) was conducted from 25 to 800°C under both N_2 and air separately with ramp rate of $10^\circ\text{C}/\text{min}$ and flowrate of $100 \text{ mL}/\text{min}$. Surface chemical structure of GA was analyzed with XPS (Thermo K-Alpha).

4.2.4. Electrochemical Characterization of GA

Prior to the electrochemical characterization, nickel foams (NF, 1 cm x 2 cm) were washed with acetone and 0.1 M HCl with sonication and washed with distilled water in between, followed by air drying. Approximately 1 mg circular GA (diameter: 0.5 cm, length: 0.2 cm) was cut with a blade. and pressed onto precut and cleaned NF. Then, NF loaded with GA was immersed in electrolyte solution overnight to ensure complete filling of the pores. CV measurements were conducted with a 3-electrode electrochemical cell connected to a potentiostat (Biologic VSP). The working electrode was NF loaded with GA, the counter electrode was graphite rod, and the reference electrode was SCE (sat'd KCl). Electrodes were scanned between -0.9-0.1 V vs SCE at scan rates ranging from 100 to 5 mV s⁻¹. GA ink was prepared for the RDE measurements. 5.0 mg GA powder, 500 μ L distilled water, 370 μ L ethylene glycol, and 130 μ L 1 wt% nafion solution was mixed with sonication for 1 h. 1 μ L GA ink was drop-casted onto GCE and dried at 60 °C for 1 h. ORR activity measurements were conducted with the RDE setup explained in Section 2.2.7. ORR polarization curves were measured in both O₂-saturated 0.1 M HClO₄ and 0.1 M KOH separately in the potential range 0.0-1.2 V vs RHE at 5 mV s⁻¹.

4.3. Results & Discussion

4.3.1. Structural Properties of GA

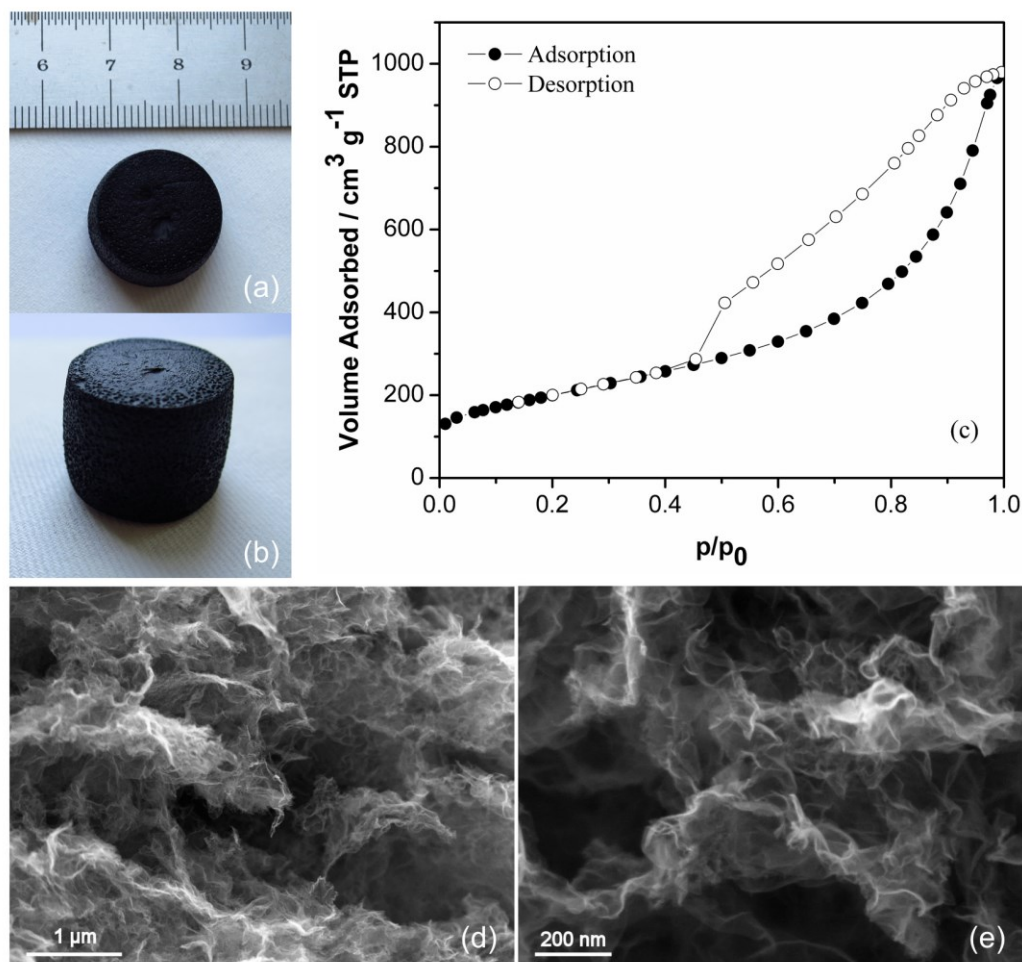


Figure 4-5 Top (a), and side (b) view images of GA. Isothermal hysteresis loops of GA (c). SEM images of GA (d,e).

After hydrothermal reaction of the GO exfoliation solution followed by supercritical CO₂ drying, black monolithic GA was obtained. Photographs of the GA monolith are presented in Figure 4-5a,b. The pore structure of the as-synthesized GA was determined using N₂ physisorption. Figure 4-5c shows the N₂ adsorption/desorption isotherms of the prepared GA. The sample had a BET surface area of 708 m² g⁻¹, a total pore volume of 1.54 cm³ g⁻¹, a micropore volume of 0.024 cm³ g⁻¹ and an average pore diameter of 5.8 nm. The nitrogen adsorption data show that this GA

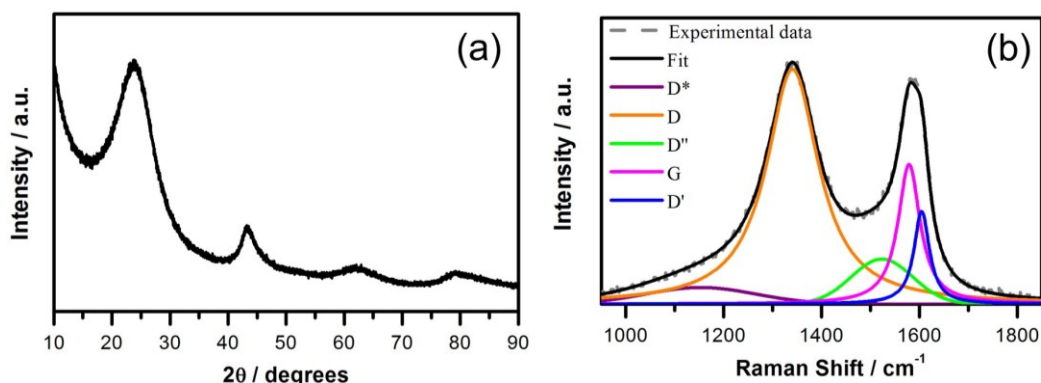


Figure 4-6 (a) XRD diagram of GA (b) Fitted Raman spectrum of GA

sample exhibits a Type IV isotherm with a H1-type hysteresis loop indicating that GA samples have a mesoporous structure. [195]

XRD diagram of GA is shown in Figure 4-6a. The diagram consists of a broad peak around $2\theta = 23.8^\circ$ giving an interlayer spacing of 0.371 nm. This spacing is much lower than that of GO indicating efficient restoration of sp^2 -hybridized network. [197] Fitted Raman spectrum of GA (Figure 4-6b) exhibits similar peaks with that of GO, although the fitting results have altered. Both ID/IG and ID'/IG increased upon conversion of GO to GA, signifying an increase in the amount of defects in the structure (Table 4-2). Furthermore, ID^*/IG and ID''/IG also have higher values than that of GO. Formation of GA results from random distribution of reduced GO layers. This caused enhancing of the ratios (ID^*/IG and ID''/IG) since D^* is related with disordered graphitic lattice and D'' with amorphous phases. [198] In comparison

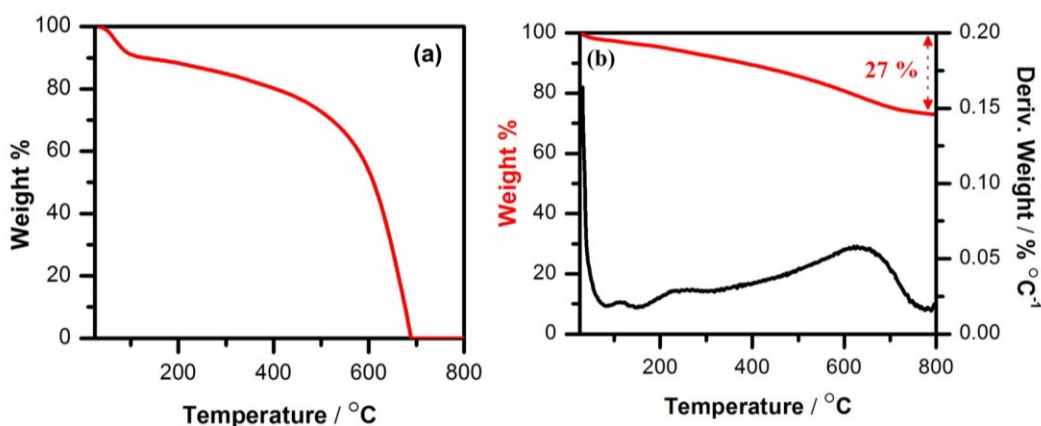


Figure 4-7 TG/DT curve of GA in (a) air (b) nitrogen. Flow rate: 100 mL min^{-1}

with GO, the red-shift in D and G band positions in GA results from the deoxygenated GO layers in GA. [199]

Table 4-2 Structural parameters of GA calculated from Raman spectrum

Sample	I_D/I_G	I_{D^*}/I_G	$I_{D''}/I_G$	$I_{D'}/I_G$	D (cm^{-1})	G (cm^{-1})
GA	1.68	0.12	0.32	0.66	1341	1579

To investigate thermal properties of GA, TG analysis were conducted in both N_2 and air. Figure 4-7a shows TG curve of GA where gradual decrease in weight is observed until 600 °C accompanied with a sharp decrease around this temperature prior to complete decomposition. Thus, synthesized GA exhibited high thermal stability in air which is previously observed in nitrogen doped GA. [200] Figure 4-7b presents TG/DT curves of GA in N_2 . Until 800 °C, 27 % of the initial mass is reduced substantially. This decrease indicates the removal of oxygen functional groups. [201]

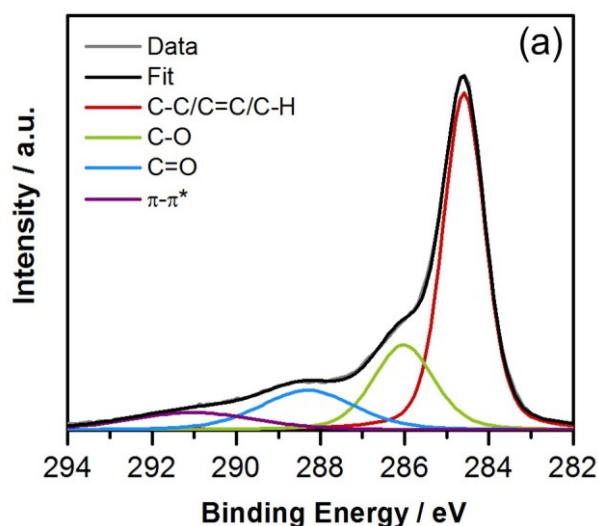


Figure 4-8 XPS C 1s spectrum of GA

Figure 4-8a shows XPS C 1s spectrum of GA. The spectrum is deconvoluted into three peaks, as in that of GO. The relative intensities of C-O and C=O (with respect to C-C) are lowered to 0.25 and 0.12 from 1.25 and 0.15, compared to GO, respectively (Section 2.3.1.). Thus, rather than C=O, eliminated functional groups are C-O during the self-assembly. Overall,

deoxygenation is validated during the hydrothermal reaction, in agreement with XRD and TGA results.

4.3.2. Electrochemical Properties of GA

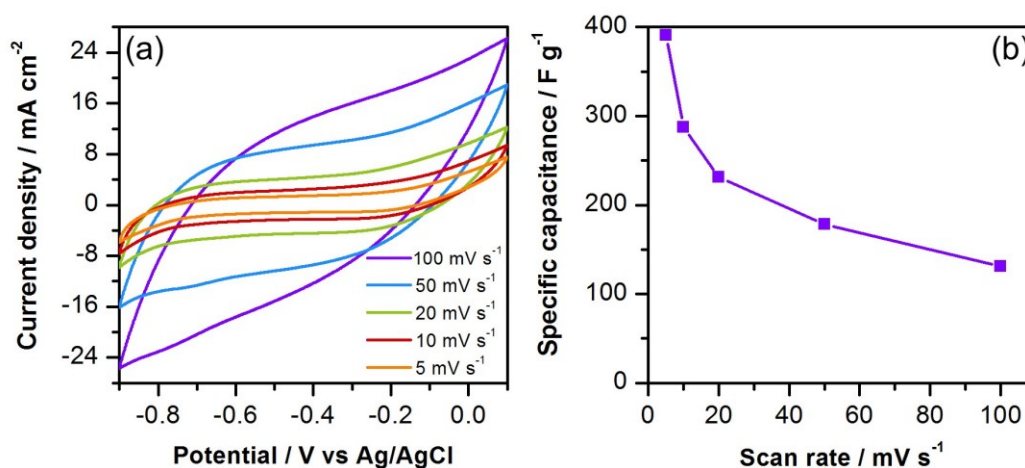


Figure 4-9 (a) Cyclic voltammograms of GA at different scan rates (b) Specific capacitance vs scan rate of GA. Electrolyte is 0.5 K_2SO_4 .

To evaluate the electrochemical properties of GA, CV measurements were conducted with a piece of circular GA pressed on nickel foam. Figure 4-9a shows CV curves of GA at different scan rates. Distorted rectangular shape of curves is observed indicating pseudocapacitive properties. Figure 4-9b shows the corresponding specific capacitance values. GA exhibited specific capacitance of 131, 178, 231, 287, and 390 F g^{-1} at 100, 50, 20, 10, and 5 mV s^{-1} , respectively. The enhanced specific capacitance obtained at 5 mV s^{-1} is higher than almost all the GAs reported in the literature (Table 4-1). This high electrochemical performance is mainly due to the higher BET surface area of GA produced ($708 \text{ m}^2 \text{ g}^{-1}$) since our aerogels were dried with scCO_2 . The studies included in Table 4-1 utilize freeze-drying as the drying method which results in lower surface area values and distorted pore structure due to destructive nature of ice formation. The capacitance value of an electrode is directly proportional with the surface area for electrostatic charge storage (EDLC), and higher surface area results in efficient charge transfer for surface redox reactions (pseudocapacitor). Thus, higher surface area provides higher electrochemical performance.

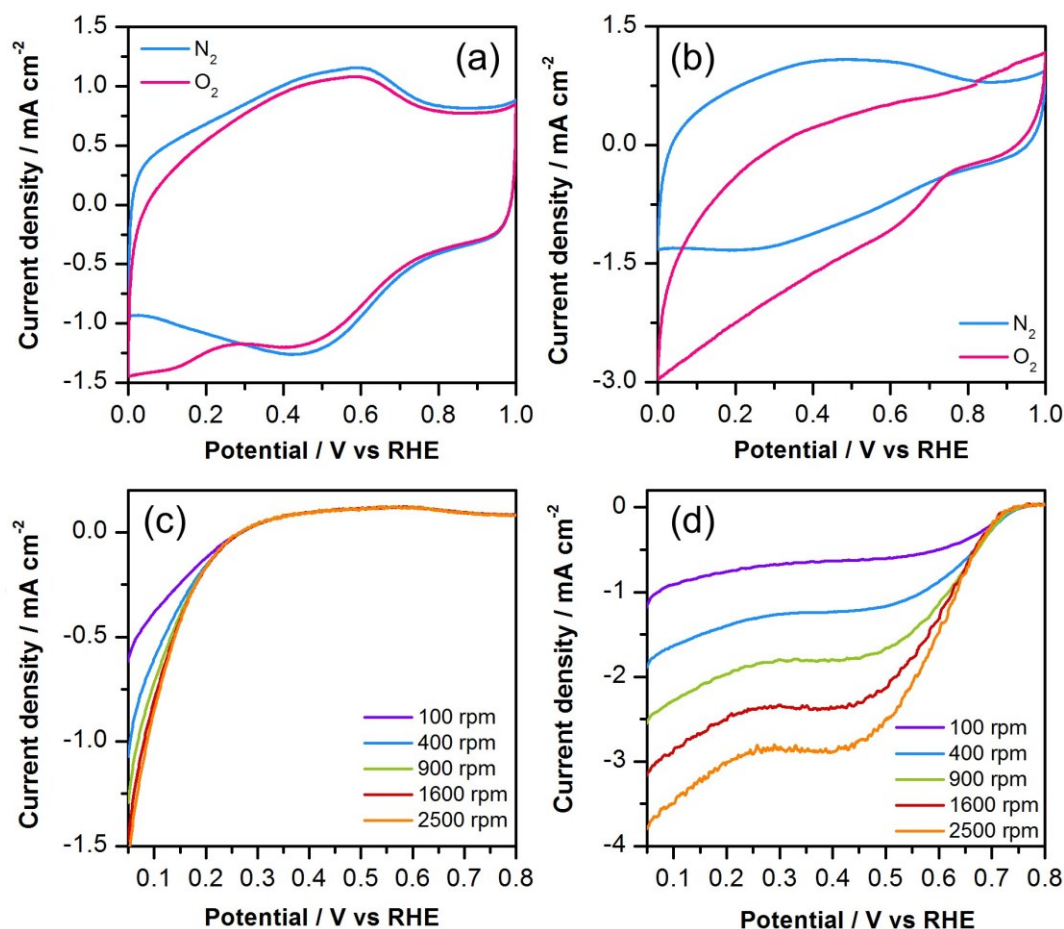
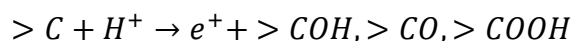


Figure 4-10 Cyclic voltammograms of GA in N_2 and O_2 saturated (a) 0.1 M $HClO_4$ (b) 0.1 M KOH at 50 mV s^{-1} , ORR polarization curves of GA in O_2 saturated (c) 0.1 M $HClO_4$ (d) 0.1 M KOH at 5 mV s^{-1}

For evaluation of electrocatalytic activity of GA towards ORR, CV and RDE measurements were conducted. Figure 4-10a,b show CV curves of GA in 0.1 M $HClO_4$ and 0.1 M KOH solutions. Obtained curves in N_2 -saturated solutions contain broad symmetric peaks. These peaks are assigned to pseudocapacitive redox peaks of oxygen functional groups in reduced GO and resulting from the following reaction [46]:



According to the above equation, new functional groups are formed during anodic sweep, and previously formed functional groups reduce to C-C bonds in the cathodic sweep. Upon switching to O_2 in $HClO_4$ solution results in appearance of a reduction wave around 0.2 V in Figure 4-10a. RDE measurements in the same solution validated the weak (almost negligible) electrocatalytic

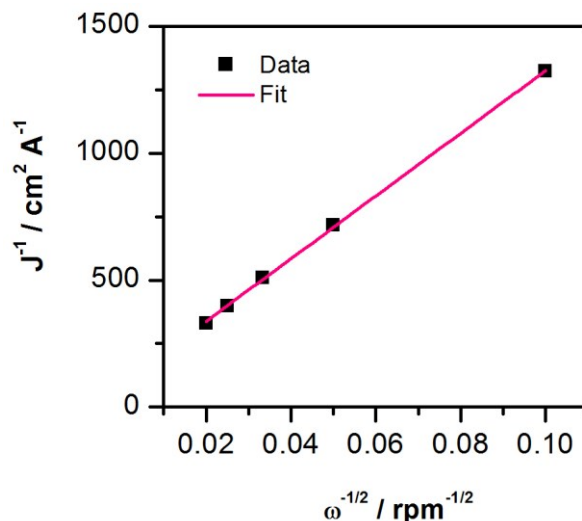


Figure 4-11 Koutecky-Levich plot of RDE curves of GA in 0.1 M KOH. Currents are read from 0.2 V (vs RHE)

activity of GA towards ORR in acidic solution. The situation is quite different in alkaline environment. The ORR wave shifts to 0.7 V (vs RHE) when CV is taken in O₂-saturated KOH solution (Figure 4-10b) indicating much higher electrocatalytic activity. RDE curves at different rotation speeds exhibited well-defined waves with increasing current densities with rotation speeds. The half-wave potential at 1600 rpm is 0.61 V (vs RHE) which is almost 200 mV more negative than that of nitrogen-doped graphenes reported in the literature. [68] The correlation between current density and the rotation speed is analyzed by plotting j^{-1} vs $\omega^{-1/2}$ which is also known as the Koutecky-Levich (K-L) plots. The linearity of K-L plot in Figure 4-11 indicated sluggish reaction kinetics. From the slope of K-L plot (B), electron transfer number per oxygen molecule can be calculated according to the following equation:

$$B = 0.2nFC_0(D_0)^{\frac{2}{3}}\nu^{-\frac{1}{6}}$$

where n is the electron transfer number, F is the Faraday constant (96485 C mol⁻¹), C_0 is the bulk concentration of oxygen (1.2x10⁻⁶ mol cm⁻³), D_0 is the diffusion coefficient of oxygen in 0.1 M KOH (1.9x10⁻⁵ cm² s⁻¹), ν is the kinematic viscosity (0.01 cm² s⁻¹), and 0.2 is used as correction number when the rotation speed is expressed as rpm. [124] From Figure 4-11, n is calculated as 2.28 suggesting GA follows a 2-electron pathway for ORR in alkaline solution.

4.4. Conclusions

In this chapter, synthesis of graphene hydrogels via one-step hydrothermal treatment of GO solution was presented. These hydrogels were converted to aerogels by scCO₂ drying. Obtained aerogels had large BET surface areas around 700 m² g⁻¹, resulting from the special drying technique. Simultaneous reduction of GO was observed along with hydrogel formation, confirmed by XRD and XPS. Produced GA was thermally stable until 800 °C under N₂ environment, whereas complete combustion was observed in air around 600 °C.

Electrochemical characteristics of GA was further investigated by CV and RDE measurements. Supercapacitor electrodes were produced by pressing a piece of GA monolith onto nickel foam. At 5 mV s⁻¹, high specific capacitance of 390 F g⁻¹ was obtained. Electrocatalytic activity of metal-free GA towards ORR was measured with RDE. In acidic electrolyte (0.1 M HClO₄), GA exhibited negligible ORR activity whereas in alkaline electrolyte (0.1 M KOH), electrocatalytic activity was observed with a E_{1/2} of 0.61 V vs RHE.

Chapter 5: Graphene Aerogel Supported Nickel Nanoparticles as Electrocatalysts for Oxygen Evolution Reaction

5.1. Introduction

(Photo)electrochemical water splitting is located at the center of clean and sustainable energy conversion. The cathodic reaction of water splitting, hydrogen evolution reaction (HER), produces H_2 while the anodic one, oxygen evolution reaction (OER), produces O_2 , both of which are valuable fuels for various energy devices. [202] The multistep OER requires a catalyst to drive the reaction at low overpotentials. [51] Noble metals like Ru and Ir (and their oxides) are the best electrocatalysts with their low overpotentials, albeit rare and expensive. [203] Instead, researchers focused on utilization of nonprecious metal (oxides) and achieved promising results with nickel [204], cobalt [205], manganese-based [206] electrocatalysts outperforming the commercially available electrocatalysts.

For the exploitation of the theoretical activity of electrocatalysts, dispersion on an electrically-conductive and high surface area support is essential. The choice of support is generally carbon derivatives due to their high electrical conductivity, surface area, and (electro)chemical stability. [207] Up to date, carbon cloth [208], multi-walled carbon nanotubes (MWCNT) [209,210] MOF derived graphenes [211,212], and N-doped graphene film [213] have been decorated with nickel (oxide) nanoparticles and used as OER electrocatalysts. Among the aforementioned carbon derivatives, graphene aerogels (GAs) are promising candidates as support materials due to their high electrical conductivity and superior surface area. [138] GAs are composed randomly stacked graphitic domains in a 3D network which are generally synthesized via hydrothermal reaction of graphene oxide (GO) solutions. [157] Consequently, a considerable amount of oxygen functional group remains which can act as anchoring sites for the catalysts. [214]

In this chapter, detailed investigation on nickel loaded GA structures are presented by using different possible crosslinkers to bind nickel to GA skeleton. Ni/GAs are synthesized via one-step hydrothermal reaction of Ni^{2+} source and GO in presence of the crosslinkers. Various amides (thiourea, urea, acetamide) and aminoacids (L-cystine, glycine, L-alanine, L-threonine) with $-\text{NH}_2$ moieties are utilized. Furthermore, nickel loadings are altered by changing the initial Ni:GO ratio with the Ni/GAs synthesized with urea. For the formation of Ni nanoparticles, powders are thermally reduced under H_2/He environment. Particle size distribution and surface chemistry are analyzed by STEM and XPS, respectively. These Ni/GAs are later utilized as OER electrocatalysts in alkaline medium. Detailed characterizations on activity and stability are presented by means of CV and chronopotentiometry under hydrodynamic conditions.

5.2. Materials & Methods

5.2.1. Materials

All the chemicals were used as received without further purification. Graphite (natural, -200 mesh, 99.9995 %), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98.0%), KOH (ACS reagent grade), thiourea (ACS reagent grade), acetamide (99%), and NaNO_3 (99 %) were obtained from Alfa Aesar. KMnO_4 , ethanol (EMPROVE), NaOH (>99.0%), L-cystine (>99%), glycine (>99.7%), L-alanine (>99%), urea (>99%), L-threonine (>99%), and H_2O_2 (30 %) were purchased from Merck Millipore. H_2SO_4 (95-97 %), nafion® perfluorinated resin solution (5 wt% in lower aliphatic alcohols and water), and HCl (37 %) were obtained from Sigma Aldrich. Reversible hydrogen electrode (RHE) was obtained from Gaskatel GmbH, Germany.

5.2.2. Synthesis of Ni/GA

5.2.2.1. Synthesis of Ni/GA with Addition of Various Crosslinkers

GO, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and the additives were mixed for 30 min. Total volume was 5 mL. GO concentration was fixed at 3.0 g L^{-1} at the final volume. Ni:GO ratio was 0.4 by weight. As additives; thiourea (75 mM), urea (25, 75, 150 mM), acetamide (25, 75, 150 mM), glycine (Ni:glycine

= 1:3 (mol)), threonine (Ni:threonine = 1:2, 1:3 (mol)), alanine (Ni:alanine=1:2, 1:3 (mol)) or L-cystine (Ni:cys = 1:1, 1:1.5 (mol)) was added. The pH of L-cystine solution was adjusted to 10.5 with KOH since cystine is not soluble in neutral water. [215] According to the produced gels' mechanical stability, the amounts of additives were predetermined with several experiments. The mixtures were placed in a small glass vial (12 mL of total volume) and treated at 95 °C for 24 hours. After cooling down naturally, the solvents in which the gels are suspended were replaced with acetone. After 24 hours, the solvents were decanted away, and the gels were dried in an oven at 70 °C overnight.

5.2.2.2. Synthesis of Ni/GA with Addition of Urea

GO, Ni(NO₃)₂·6H₂O, and urea were mixed for 30 min. Total volume was 40 mL. Ni:GO ratio was 0.01, 0.05, 0.1, 0.2, or 0.4 (wt). Ni:urea ratio was 1:2 (mol) in all the nickel loadings. GO concentration was adjusted as 3.0 g L⁻¹ at the final volume. The mixture was placed into home-made PTFE-lined stainless-steel reactor and put into drying oven. The temperature was raised to 180 °C and hold at this temperature for 3 h. After cooling down to room temperature naturally, black monolithic hydrogel was taken out from the reactor and placed into fresh distilled water for 24 h. Then, the water was exchanged with ethanol three times, each held in the fresh ethanol for further 24 h. The alcogel was then dried by using a sCO₂ dryer (Spe-ed SFE-15,000, Applied Separations, Inc.) at 50 °C and 12.0 MPa for 1.5 h.

For the conversion of nickel precursor in nickel/GA composite into nickel nanoparticles, thermal reduction was conducted in H₂/He environment. Crushed Ni/GA powder was placed in a crucible which was further introduced into a split-oven with both ends open. First, the powder was degassed under flowing He (200 mL min⁻¹) at 110 °C for 30 min. Then, the flowing was switched to H₂/He mixture (10:90, 200 mL min⁻¹) and ramped to 650 °C with 5 °C min⁻¹. The furnace was held at 650 °C for 2 h, followed by switching to flowing He and cooling down naturally. Obtained powders were named thereafter Ni/GA_n (where n is the Ni:GO ratio in the initial hydrogel synthesis mixture).

5.2.3. Structural Characterization of Ni/GA

Surface morphology of the powders were evaluated with FESEM (Zeiss Ultraplus) with accelerating voltage of 10 kV. STEM images of Ni nanoparticles dispersed on GA were taken with FESEM (Zeiss Ultraplus) coupled with STEM detector with accelerating voltage of 20 kV. Nickel loadings of Ni/GA composites were determined with TGA (TA Instruments TGA Q500) with flowing air/N₂ mixture (60:40). The powders were heated to 800 °C with a ramp of 10 °C min⁻¹. XPS analysis of samples were conducted with Thermo K-Alpha with Al K α source. The fittings were conducted with Avantage software.

5.2.4. Electrochemical Characterization of Ni/GA

For the electrochemical analysis, inks were prepared from mixing 5.0 mg Ni/GA powder, 870 μ L ethylene glycol, and 130 μ L 1 wt% nafion solution. The mixture was sonicated for 1 h to ensure homogeneous dispersion. 1 μ L ink was dropped onto glassy carbon electrodes (diameter: 3mm, active area: 0.0707 cm²) and dried at 60 °C for 1 h. By using the RDE setup explained in Section 2.2.7. , CV measurements were conducted. Glassy carbon loaded with Ni/GA was the working electrode, Pt sheet was the counter electrode, and RHE was the reference electrode. Electrolyte was 1.0 M KOH. To ensure saturation of electrolyte with the purging gas, electrolyte was bubbled with the flowing gas (N₂ or O₂) for at least 20 min. CV measurements were conducted in N₂ or O₂-saturated 1.0 M KOH in the potential range 0.0-1.0 V (vs RHE). For the evaluation of OER activity, RDE measurements were conducted in O₂-saturated 1.0 M KOH at 10 mV s⁻¹ and rotating speed of 1600 rpm. At least 5 polarization curves were recorded until a consistent data was obtained. OER stability measurements were conducted by chronopotentiometric measurement at 10 mA cm⁻² in O₂-saturated 1.0 M KOH for 2 h.

5.3. Results & Discussion

5.3.1. Structural Characterization of Ni/GA Composites

5.3.1.1. Ni/GA Composites Synthesized with Various Crosslinking Agents

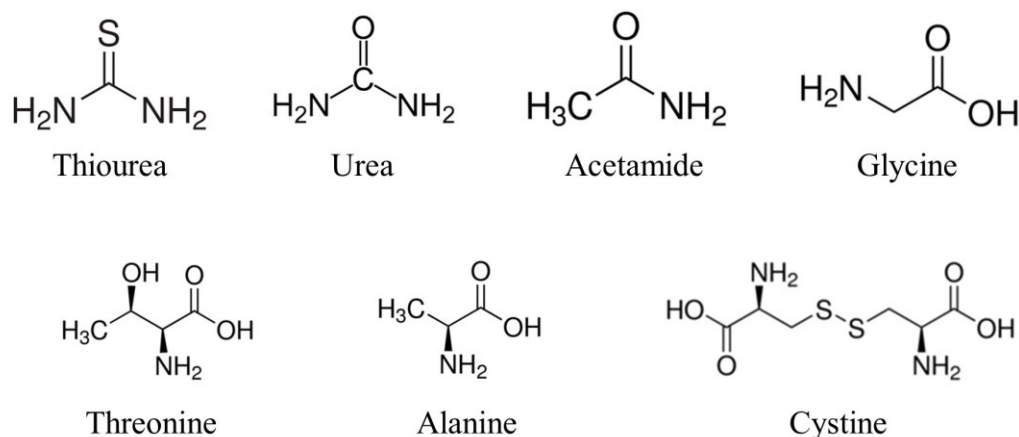


Figure 5-1 Chemical structures of the crosslinkers used in the synthesis of Ni/GA composites

The chemical structures of the crosslinkers used in this study are shown in Figure 5-1. All the chemicals contain amine group(s), whereas thiourea and L-cystine have sulfur moieties. All the aminoacids and L-cystine also have hydroxyl group(s).

Digital images of Ni/GA composites obtained by the addition of various crosslinkers are given in Figure 5-2. As control experiment, Ni/GA was synthesized without addition of any crosslinkers, which resulted in formation of black dispersion, not a hydrogel. Addition of all the additives resulted in formation of black cylindrical monoliths with different volumes. The most stable hydrogel is formed by the addition of thiourea (vial #1 in Figure 5-2). For the determination of Ni loadings, only the hydrogels that were the most stable (mechanically) were used (vials #1, 2, 8, 9, and 12) compared to others.



Figure 5-2 digital images of Ni/GA composites synthesized with various crosslinkers (1) 75 mM thiourea (2) 75 mM urea (3) 25 mM urea (4) 150 mM urea (5) 75 mM acetamide (6) 25 mM acetamide (7) 150 mM acetamide (8) glycine (Ni:gly=1:3 (mol)) (9) threonine (Ni:thr=1:3 (mol)) (10) alanine (Ni:ala=1:3 (mol)) (11) cystine (Ni:cys=1:1 (mol)) (12) L-cystine (Ni:cys=1:1.5 (mol)) (13) alanine (Ni:ala=1:2 (mol)) (14) threonine (Ni:thr=1:2 (mol)) after reaction at 95 °C for 24 h

The nickel loadings were determined via TGA measurements. It has been previously shown that GA completely decomposes when thermally treated under air (Figure 4-7a). During heating of Ni/GA composites under air, nickel precursor (cation, oxide, or hydroxide) oxidizes to NiO, while GA decomposes to form CO and CO₂ gases. [216,217] Remained weight is assumed to be sole NiO. TG curves of the composites are shown in Figure 5-3a and corresponding NiO loadings are tabulated in Table 5-1. The highest nickel amount was obtained by addition of urea, followed by L-cystine and glycine.

Table 5-1 NiO loadings of Ni/GA composites with addition of various crosslinkers calculated from TGA measurements

Additive	NiO loading (wt%)
Thiourea	7.0
Urea	31.5
Glycine	16.2
Threonine	9.0
L-Cystine	24.3

FESEM images of Ni/GA composites are shown in Figure 5-4. Different crosslinkers resulted in formation of porous graphene structures with changing morphologies. No distinguished nickel

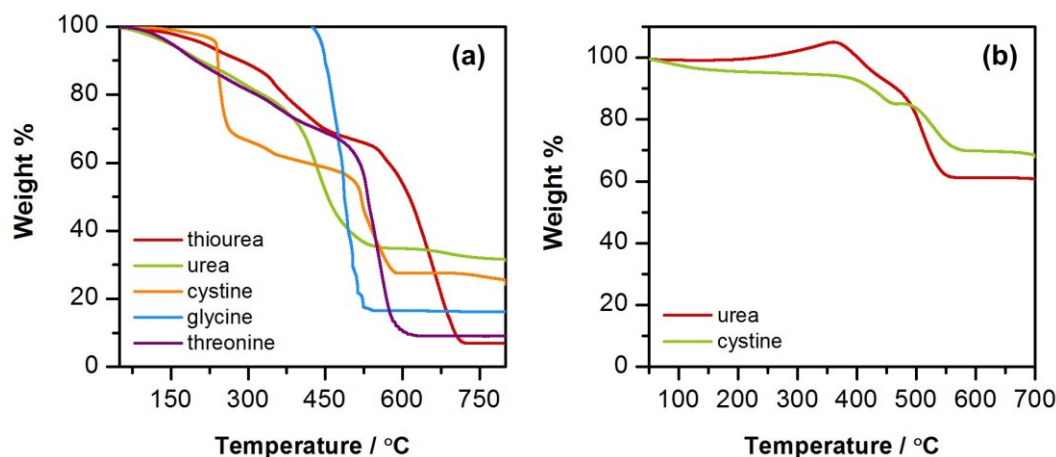


Figure 5-3 TG curves of (a) Ni/GA synthesized with different additives at 95 °C 24 h (b) 180 °C 3 h and thermally reduced at 650 °C 2 h

particles were observed in any of the images. In L-cystine added Ni/GA, the surface is covered with rod-like particles (Figure 5-4f).

Since urea and cystine addition favored nickel incorporation into GA network (validated with TGA), additional experiments were performed by repeating the synthesis under hydrothermal conditions at 180 °C for 3 h in closed reactors. Furthermore, these composites were thermally reduced to obtain nickel nanoparticles due to absence of particles in FESEM images of Ni/GA composites (Figure 5-4). TG curves of these thermally reduced composites are shown in Figure 5-3b and NiO loadings are tabulated in Table 5-2. As seen from Table 5-2, NiO loadings of the composites are much higher than that of synthesized at 95 °C even though the duration was much shorter (3 vs 24 h).

Table 5-2 NiO loadings of Ni/GA with urea or L-cystine. TG curves were recorded after thermal reduction at 650 °C for 2 h in H₂/He mixture (10:90)

Additive	NiO loading (wt%)
L-Cystine	69.6
Urea	60.9

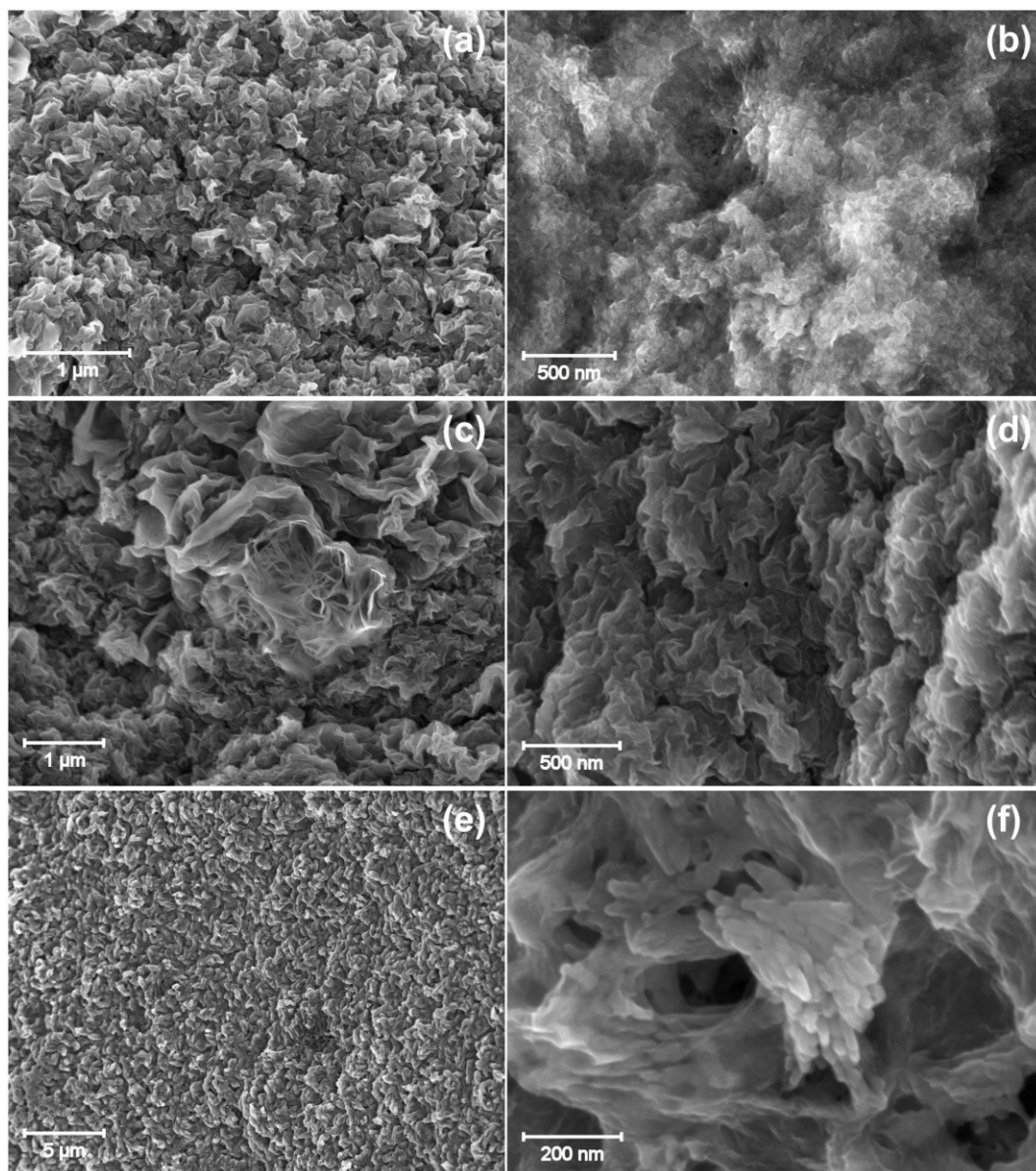
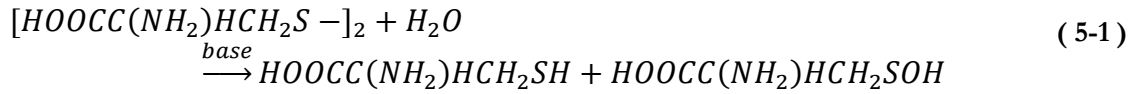


Figure 5-4 FESEM images of Ni/GA composites synthesized with addition of (a) thiourea (b) urea (c) glycine (d) threonine (e,f) L-cystine at 95 °C for 24 h

FESEM images Ni/GA synthesized at 180 °C are shown in Figure 5-6. NiS nanoparticles (as validated with EDX) with approximate diameters of 100 nm dispersed on GA are observed after reaction (Figure 5-6a,b). L-cystine, two cysteine molecules bound with a disulfide (S-S) bond, is insoluble in water and can only be dissolved when the pH is lower than 2.5 or higher than 10.5. [215] Thus, as explained in Section 5.2.2.1. , L-cystine solution was pre-prepared at pH 10.5 and the resulting GO+Ni+L-cystine solution is basic. Growth of NiS particles can be explained by the cleavage of L-cystine dimer to form two cysteine molecules by base-hydrolysis at high

temperatures (180 °C) and precipitation of metal sulfide by the following reactions consequently [218,219]:



Thermally reducing L-cystine added Ni/GA composite leads to formation of microscopic sulfur compounds that contains large amount of potassium compared to non-reduced one (Figure 5-5). Addition of urea to Ni/GA composite and subsequent reduction resulted in production of well-dispersed Ni nanoparticles with approximate diameters of 25 nm (Figure 5-6e,f).

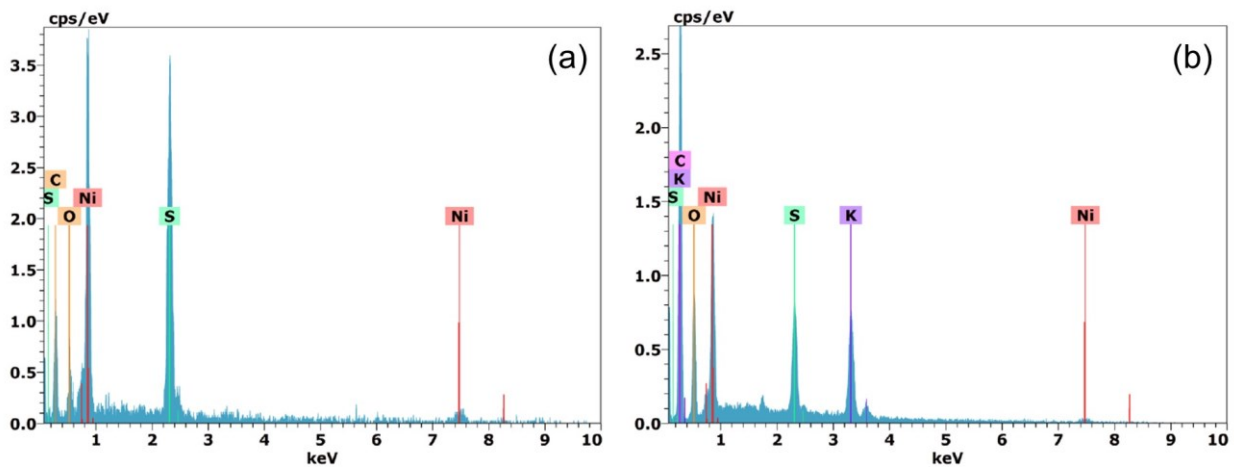


Figure 5-5 EDX spectrum of (a) Ni/GA with L-cystine synthesized at 180 °C (b) Ni/GA with L-cystine synthesized at 180 °C and thermally reduced at 650 °C

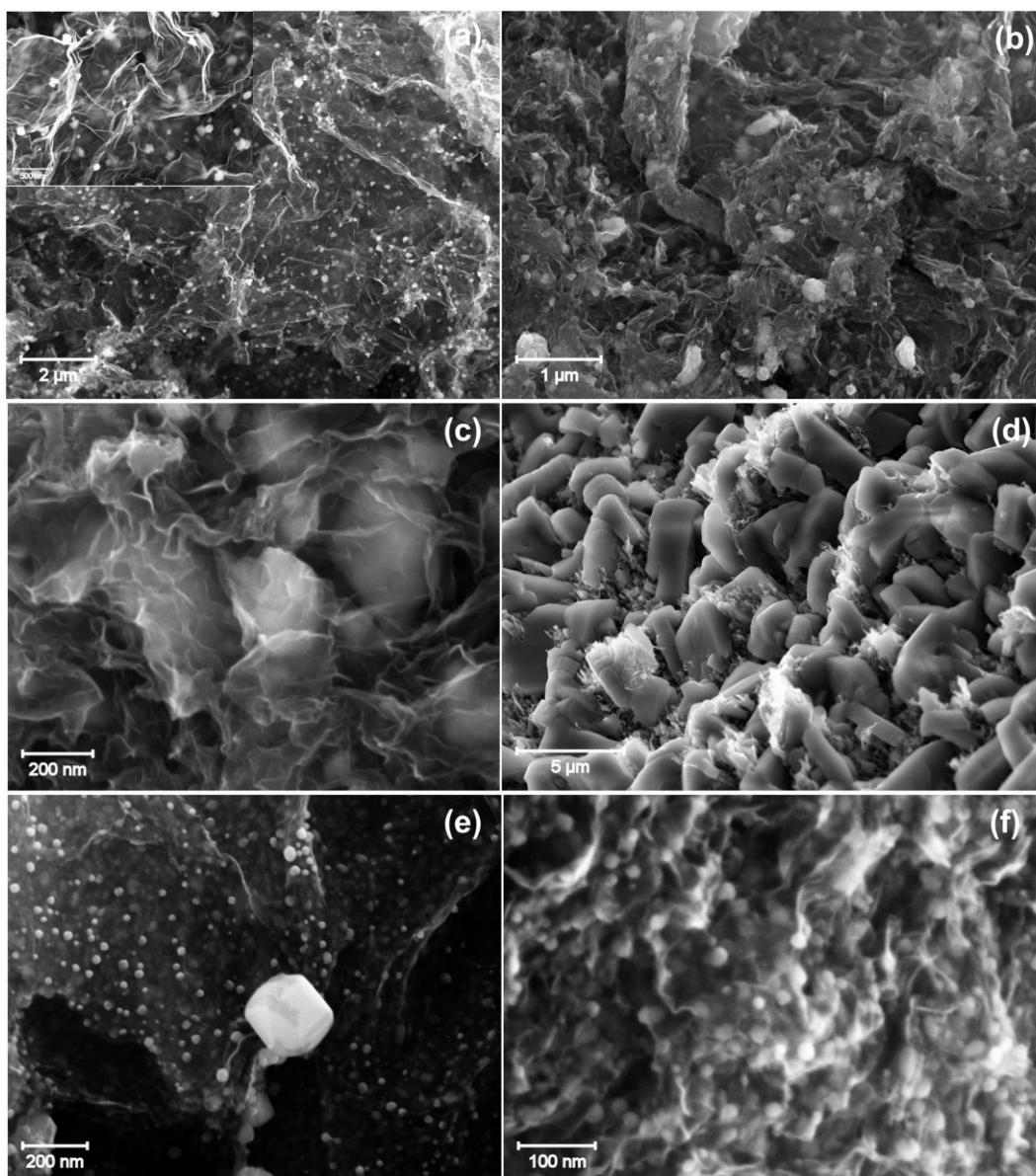
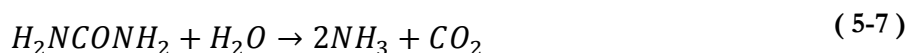


Figure 5-6 FESEM images of Ni/GA composites synthesized at 180 °C for 3 h with addition of (a-d) cystine or (e,f) urea. (c-f) were recorded after thermal reduction.

5.3.1.2. Ni/GA Composites Synthesized with Urea

Since addition of urea resulted in the highest nickel incorporation into GA structure (loading) and well-dispersed nanoparticles in Section 5.3.1.1. , the composites synthesized with urea are investigated in detail.

Figure 5-7 presents schematic representation of the synthesis route for Ni loaded GAs. The hydrothermal reaction of the solution containing GO, Ni^{2+} source, and urea results in formation of $\text{Ni}(\text{OH})_2$ as a result of continuous supply of hydroxyl ions by decomposition of urea [220,221]:



The presence of $Ni(OH)_2$ is further confirmed by EDX measurements. Figure 5-8a shows FESEM image of $Ni/GA_{0.4}$ before the thermal reduction. No distinguished particles are observed, even at higher magnifications. Nevertheless, the corresponding EDX spectrum revealed that a considerable amount of nickel and oxygen is present in the structure. After thermal reduction at 650 °C, well-dispersed nickel nanoparticles are obtained, along with a few agglomerated ones (Figure 5-8b). In the corresponding EDX spectrum, oxygen amount is diminished suggesting thermal deoxygenation of GA and conversion of $Ni(OH)_2$ into Ni.

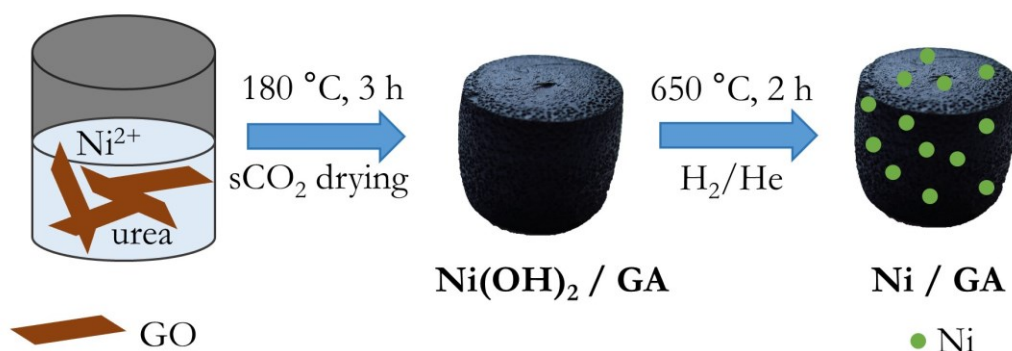


Figure 5-7 Schematic representation for the synthesis of Ni/GA

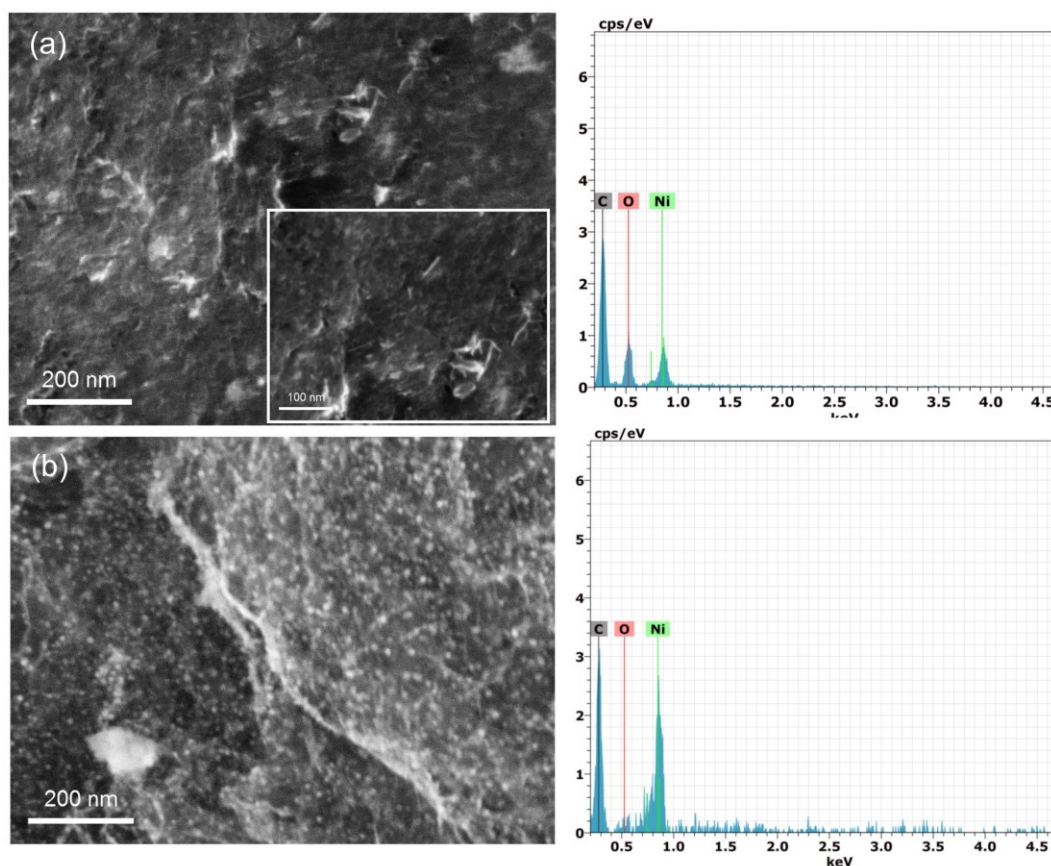


Figure 5-8 FESEM images and corresponding EDX spectra of Ni/GA_{0.4} (a) before (b) after thermal reduction

Table 5-3 Ni loadings of Ni/GA composites synthesized with urea determined via TGA. TGA measurements were conducted after thermal reduction at 650 °C

Ni:GO ratio (wt)	NiO loading (wt%)	Ni loading (wt%)
0.01	1.98	1.56
0.05	7.48	5.88
0.1	15.3	12.0
0.2	28.7	22.6
0.4	50.9	40.0

Ni loadings determined via TGA measurements for five different initial Ni:GO ratios (Figure 5-9, Table 5-3). The conversion of Ni into NiO during oxidation in air is further validated by FESEM/EDX analysis after TGA (Figure 5-10). During oxidation and decomposition of GA

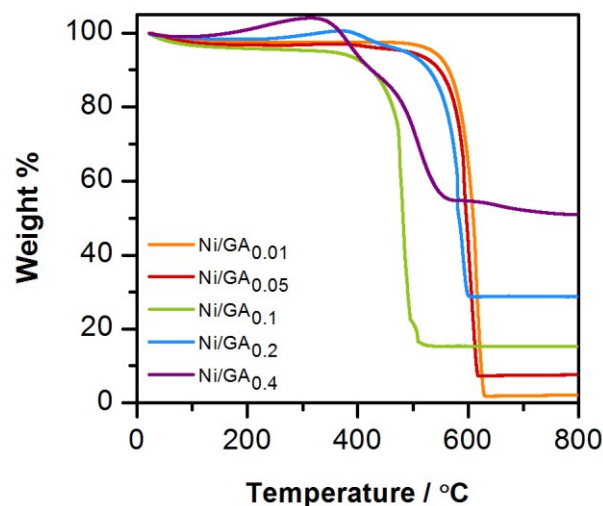


Figure 5-9 TG curves of Ni/GA with different nickel loadings. TG curves were recorded in air/N₂ mixture, Ramp: 5 °C min⁻¹, Flow rate: 100 mL min⁻¹

skeleton, NiO particles came together and grew to form particles with diameters of 200-300 nm for low Ni loadings, which were smaller (50-100 nm in diameter) for higher loadings. Previous works also showed that heating Ni to 800 °C transforms it into NiO which is proved by XRD. [217] As seen from , Ni amount can be easily modified by tuning the initial Ni:GO ratio in a highly controlled fashion. High amount of nickel (up to 40 wt%) can be incorporated into GA structure by using urea as the hydroxyl ion generator.

Figure 5-11a presents XPS spectra of Ni/GA composites with different nickel loadings. All the spectra consist of four peaks: C-C/C=C/C-H, C singly bound to oxygen, C doubly bound to oxygen, and π - π^* shake-up at binding energies of 284.4, 285.8, 287.8, and 291.0 eV, respectively. [195] The relative intensities of the functional groups (normalized to C-C peak) decreased significantly compared to bare GA (Figure 4-8a). Thus, thermal deoxygenation of GA took place along with growth of Ni nanoparticles during thermal reduction under H₂/He environment. Nevertheless, the amounts of functional groups are similar in all the Ni/GA indicating that the reduction of GA is not influenced by the amount of nickel in the structure. XPS Ni 2p spectra of Ni/GA_{0.01} and Ni/GA_{0.05} show no distinguishable peaks (Figure 5-11b). Upon increase in nickel

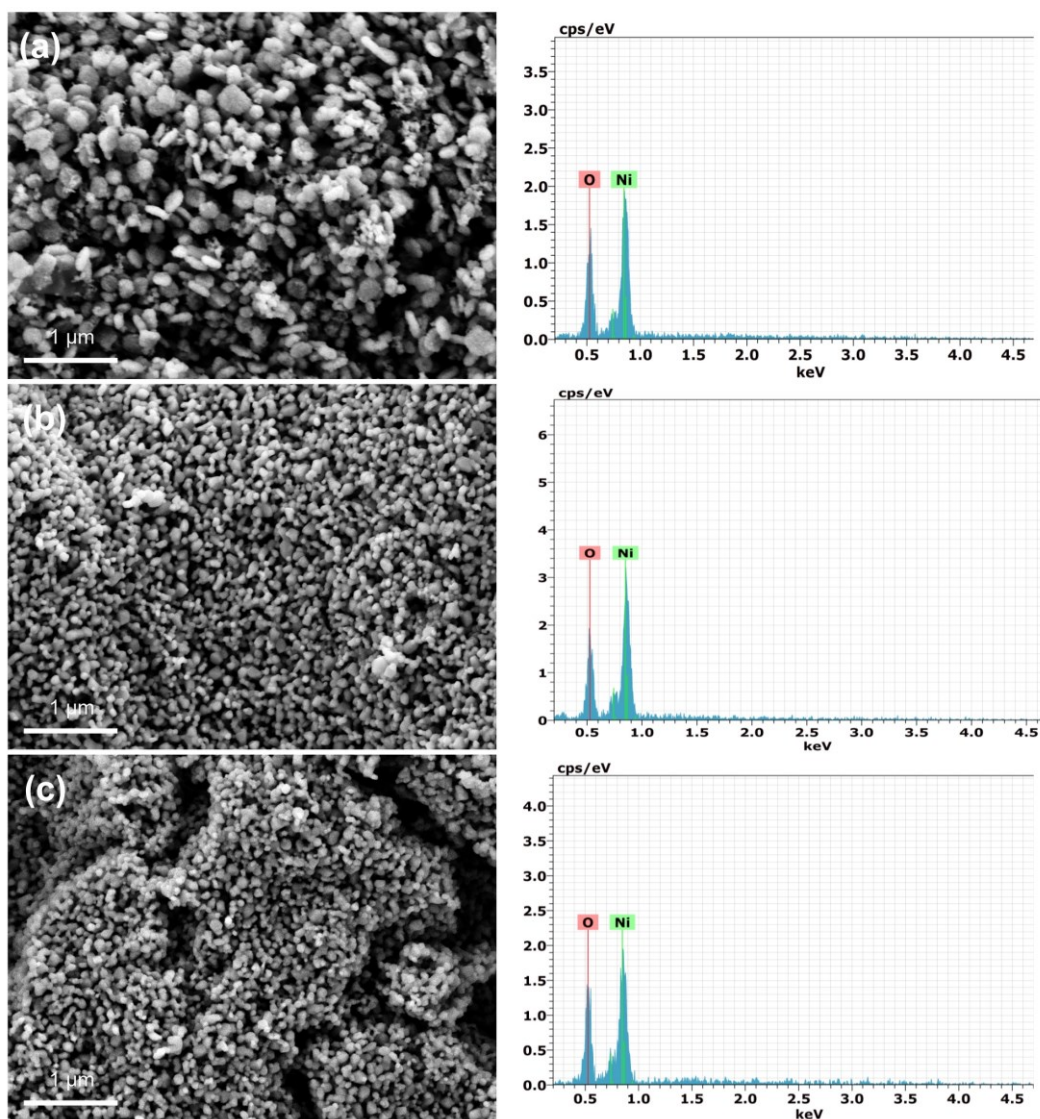


Figure 5-10 FESEM image and the corresponding EDX spectrum of (a) Ni/GA_{0.01} (b) Ni/GA_{0.1} (c) Ni/GA_{0.4}

loading, a broad Ni 2p peak arised (855 eV) accompanied with a broad satellite above the principal line (861 eV). These binding energy values matches with that of NiO. [102] In Ni/GA_{0.2} and Ni/GA_{0.4}, a new sharp peak appeared at 852.7 eV which is metallic Ni. Thus, the presence of nickel nanoparticles covered with an oxide layer is validated. Valence band (VB) spectroscopy is further utilized for the analysis of the evolution of density of states (DOS) near the Fermi level (E_F). For graphite, VB spectrum is divided into three regions: 2-12 eV for C 2p, 12-22 eV for C 2s, and >20 eV for O 2s valence electrons. [84,222,223] In the low Ni containing samples (Ni/GA_{0.01} and

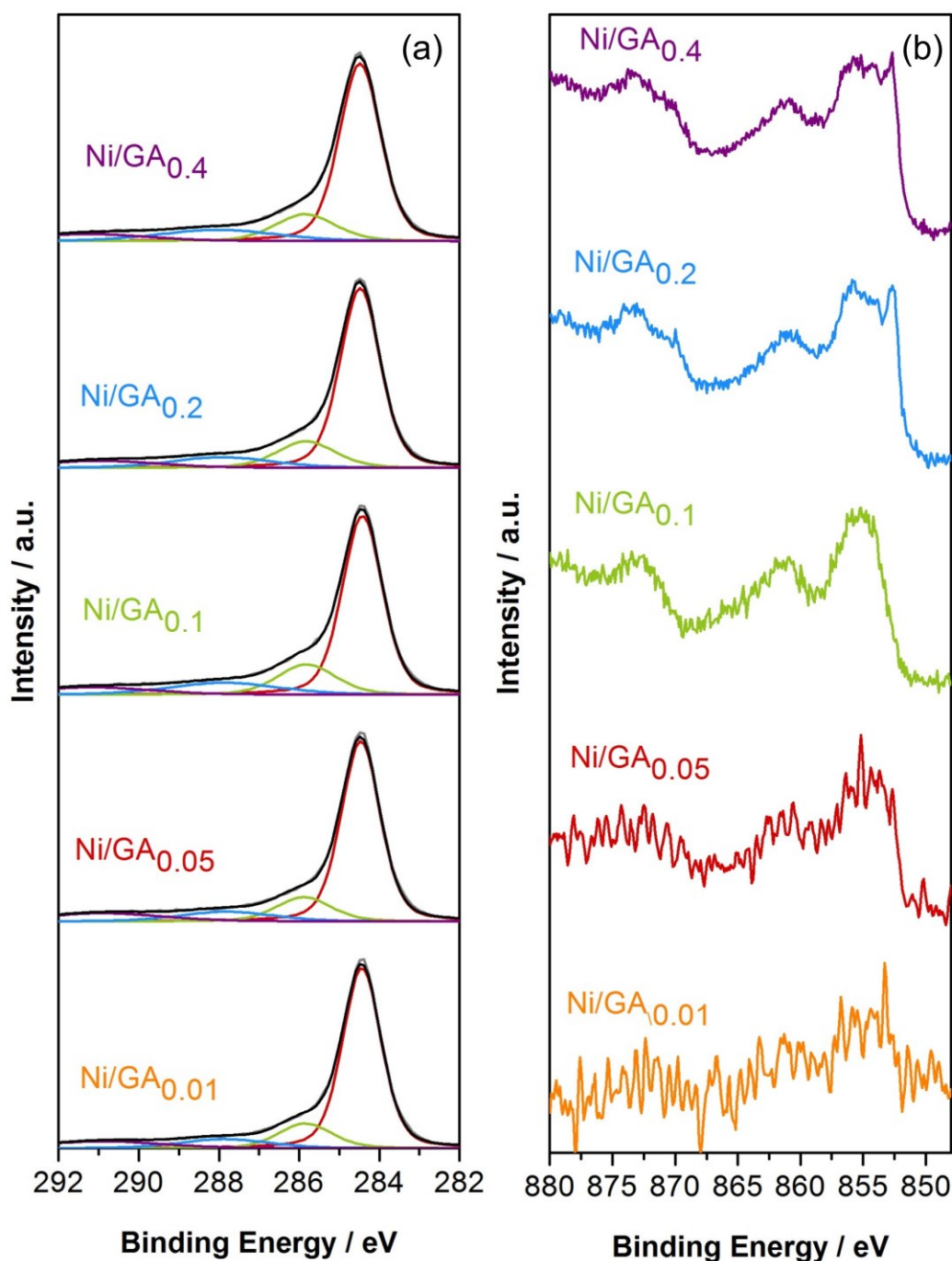


Figure 5-11 XPS (a) C 1s (b) Ni 2p spectra of Ni/GA with different nickel loadings

Ni/GA_{0.05}), VB spectra is dominated by the characteristic features of rGO, a broad shoulder around 9 eV and band located between 25-30 eV (Figure 5-12a). The former belongs to C 2p-σ in graphitic carbons and the latter is O 2s band representing the remaining oxygen functional groups after thermal reduction. [84] Upon increase in nickel loading, a substantial rise in DOS at EF is observed. The rise is the steepest in Ni/GA_{0.4} with the highest nickel content (Figure 5-12b). The

progressive increase in DOS at the vicinity of E_F with increase in Ni content proves that the metallicity of Ni/GA is enhanced by addition of nanoparticles, suppressing the effect of conjugated π -bonds in rGO. [84,224]

STEM images of Ni/GA samples are shown in Figure 5-13. The images of Ni/GA_{0.01} and Ni/GA_{0.05} could not be obtained since no particle is encountered during the analysis, probably due to low loading of these samples. In all the images, highly-dispersed nickel nanoparticles are observed on individual graphene layers. The average particle size is around 5-10 nm, regardless of nickel loading on GA. Thus, small nanoparticles that are resistant to sintering were obtained by a one-pot hydrothermal route.

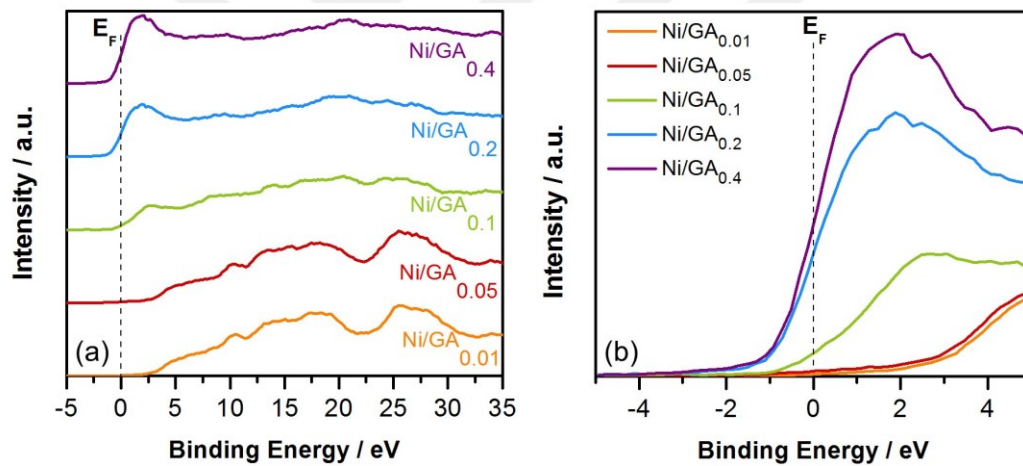


Figure 5-12 (a) High-resolution VB spectra for Ni/GA samples with different loadings (b) Enlarged VB spectra at the vicinity of Fermi level (E_F)

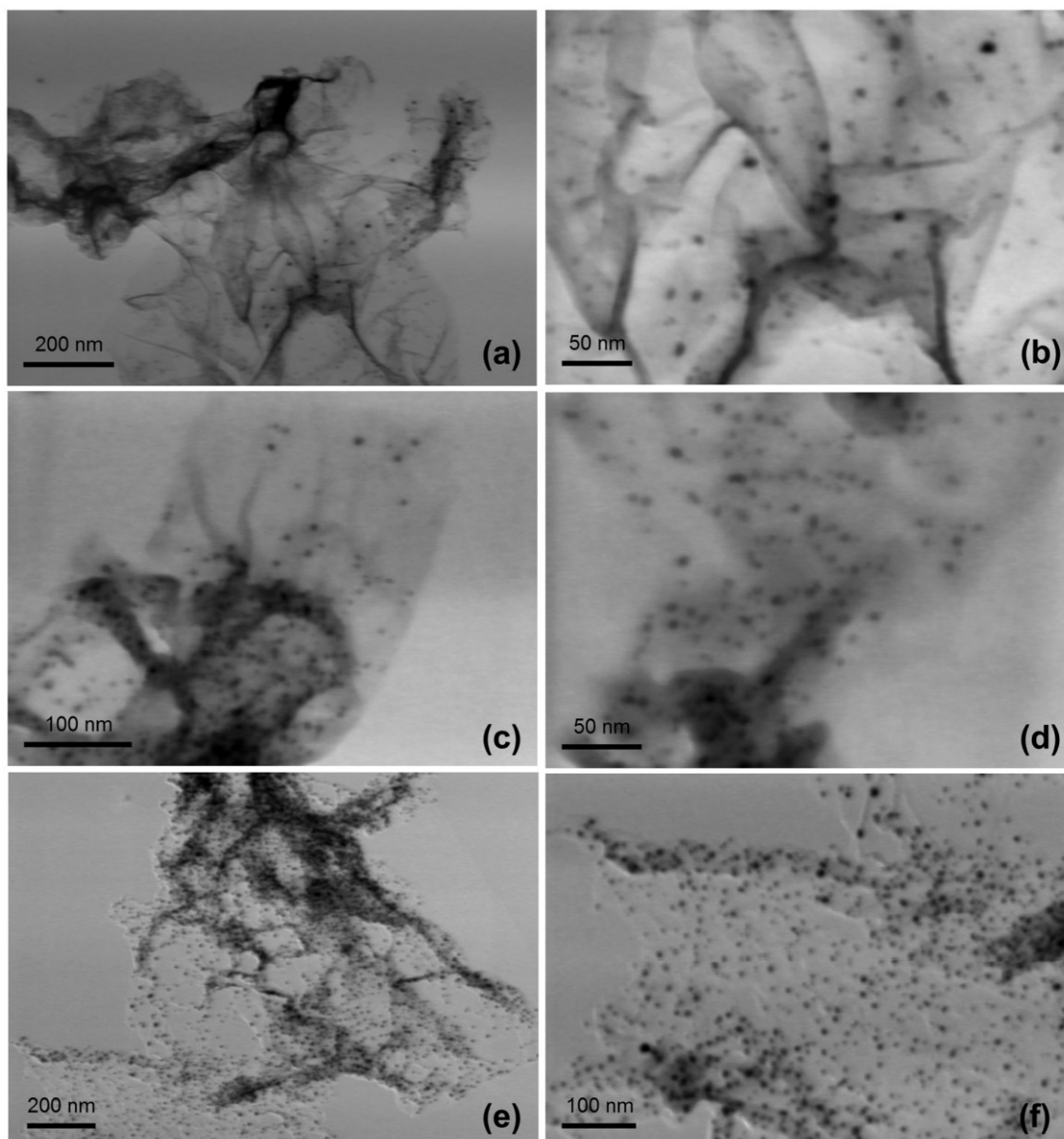


Figure 5-13 STEM images of (a,b) Ni/GA_{0.1} (c,d) Ni/GA_{0.2} (e,f) Ni/GA_{0.4}

5.3.2. Electrochemical Characterization of Ni/GA Composites

Upon immersion of Ni/GA into alkaline electrolyte (1 M KOH), immediate conversion of metallic Ni to Ni(OH)₂ is observed. In all the cyclic voltammograms of Ni/GA, a couple of redox peaks is observed in which the anodic peak is centered around 1.34 V (vs RHE) (Figure 5-14). This peak belongs to transformation of Ni(OH)₂ to NiOOH by the following equation [108]:

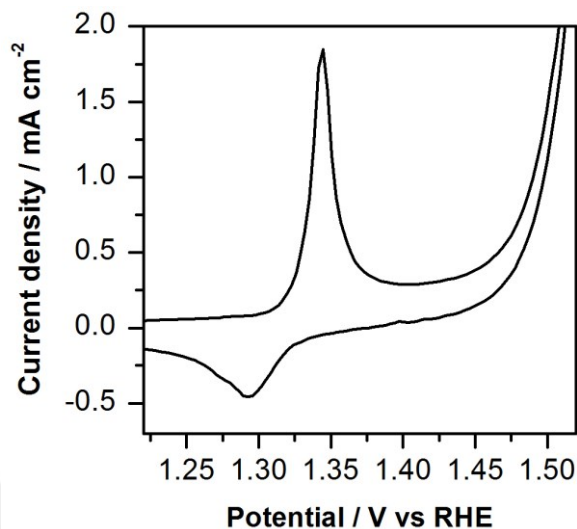
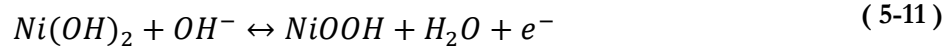
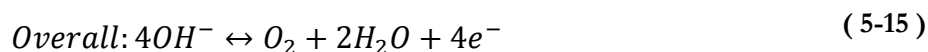
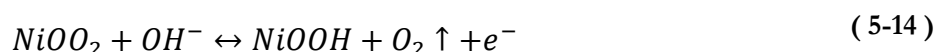
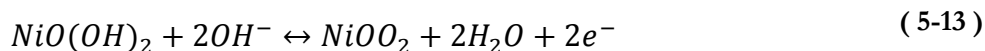
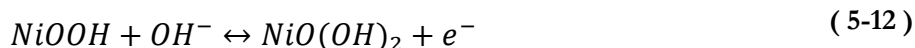


Figure 5-14 Enlarged cyclic voltammogram of Ni/GA_{0.4} in 1.0 M KOH at 10 mV s⁻¹ and 1600 rpm

Exceeding 1.50 V (vs RHE), an exponential increase in current is observed with increase in potential indicating O₂ formation from water oxidation. In alkaline environment, nickel surfaces undergo following reactions resulting in molecular O₂ evolution [225]:



Equations (5-12) and (5-13) are reversible reactions that determine the rate of overall reaction, and (5-14) is irreversible and occur fast.

Figure 5-15a shows OER polarization curves of Ni/GA with different nickel loadings. Ni/GA_{0.01} with the lowest Ni content (1.56 wt%) did not exhibit any considerable activity towards OER. Upon increase in Ni loading, substantial increase in OER activity is observed as reflected by the polarization curves (Figure 5-15a). It is apparent from Figure 5-15a that Ni/GA_{0.4} achieved the highest OER activity, reaching 10 mA cm⁻² at lower overpotentials than others. Electrochemical

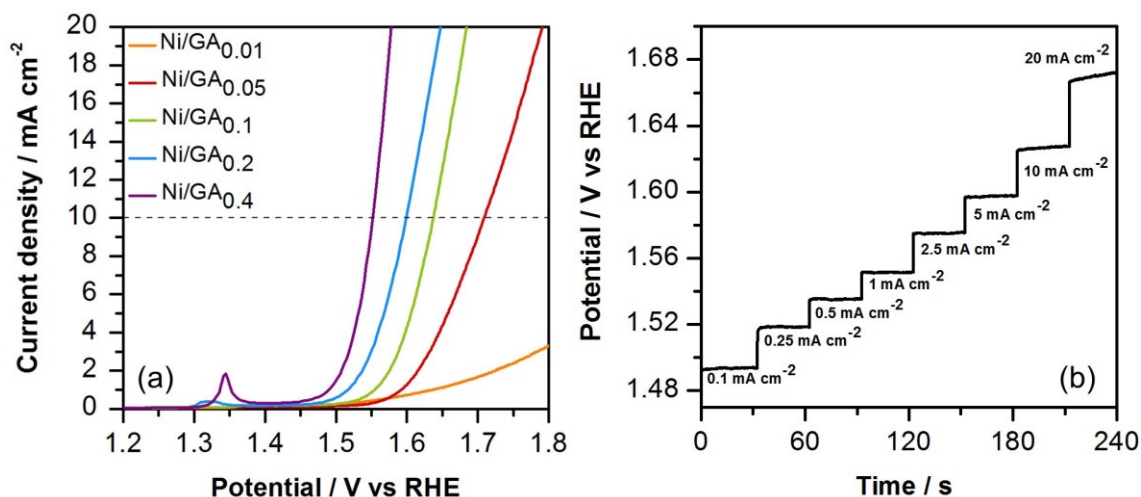


Figure 5-15 (a) OER polarization curves of Ni/GA samples with different nickel loadings in O_2 -saturated 1 M KOH at 10 mV s^{-1} and 1600 rpm, horizontal dashed line is the current density of 10 mA cm^{-2} (b) Chronoamperometric response of Ni/GA_{0.1} with current steps from 0.1 to 20 mA cm^{-2} in O_2 -saturated 1 M KOH at 1600 rpm

characteristics of all the samples are compared in Table 5-4. The onset potential is defined as the smallest potential where oxygen evolution starts and calculated from the extrapolation of OER curve through the potential (x) axis. Following the trend observed in the polarization curves, lower onset potentials are observed as the Ni content increases. Overpotentials (η) at 10 mA cm^{-2} are used to compare different electrocatalysts in the literature since this current density is expected from a 10% efficient solar water-splitting device. The lowest η value (highest OER activity) is obtained with Ni/GA_{0.4} (320 mV) which contains 40 wt% Ni. This overpotential is 110 mV more negative than that of Ni/GA reported in the literature [217], 50 mV more negative than that of 20 wt% Ir/C and 20 wt% Ru/C [206], and comparable to that of IrO₂ nanoparticles [204] indicating superior activity of our electrocatalysts (Table 5-5). In terms of the comparison of overpotentials at the same current density, the OER activity of the Ni/GA electrocatalyst is as follows: Ni/GA_{0.4} > Ni/GA_{0.2} > Ni/GA_{0.1} > Ni/GA_{0.05}.

Complementary to sweep voltammetry, chronoamperometric measurements were conducted at different current steps to simulate steady-state conditions. Figure 5-15b demonstrates a representation of these measurements for Ni/GA_{0.1}. In each current density, the potential increases steadily and stays constant throughout the 30 s current step. The steady-state values are plotted on

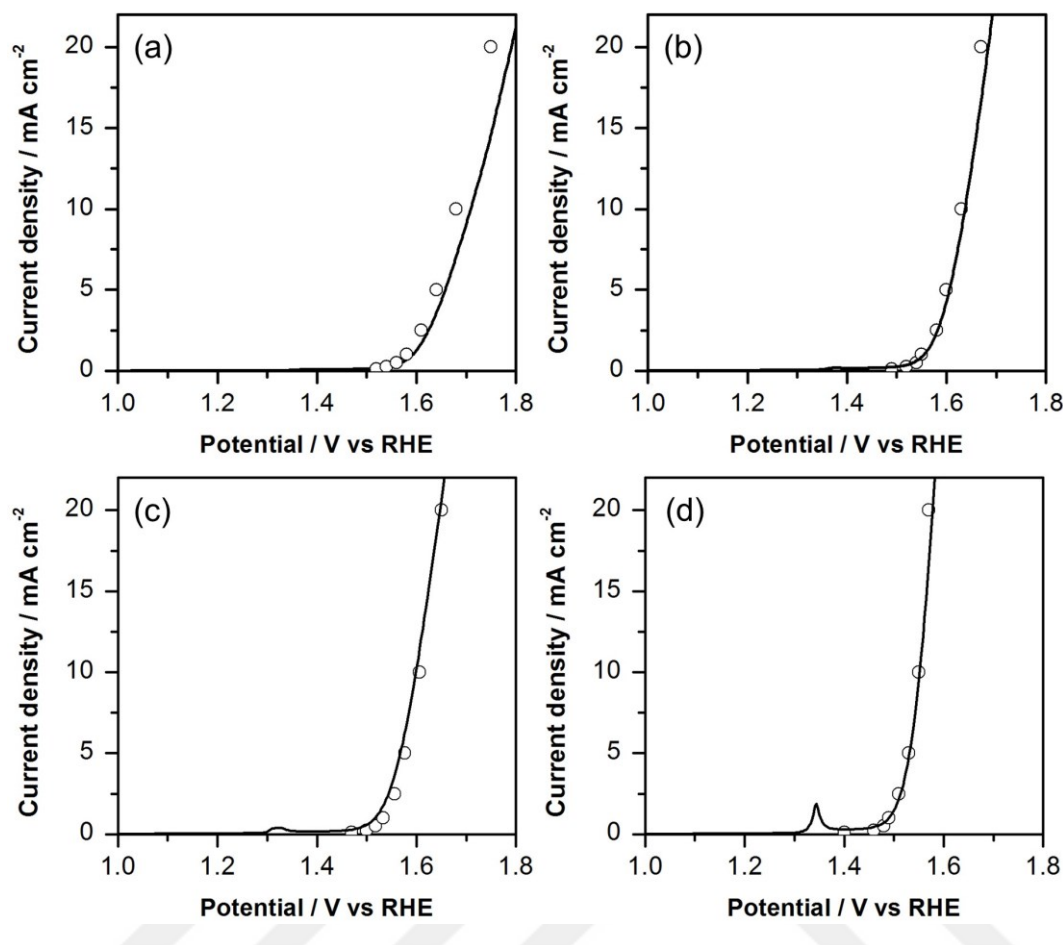


Figure 5-16 OER polarization curves of (a) Ni/GA_{0.05} (b) Ni/GA_{0.1} (c) Ni/GA_{0.2} (d) Ni/GA_{0.4} in O₂-saturated 1 M KOH at 10 mV s⁻¹ and 1600 rpm. (○) represents data of chronoamperometric steps

top of the sweep voltammograms and plotted for each electrocatalyst in Figure 5-16. The voltammograms and the data calculated from current-step measurements overlapped for each electrocatalyst, suggesting good approximation of steady-state conditions. Moreover, current densities are calculated at a specific overpotential (350 mV) and tabulated in Table 5-4. Obtained current densities increased steadily with the nickel loading. Highest current density is achieved with Ni/GA_{0.4} (21.0 mA cm⁻²) which is 20 times higher than that of NiO_x and CoO_x, and comparable to NiFeO_x electrocatalyst reported in the literature. [226] Gradual decrease in overpotentials at 10 mA cm⁻² and increase in current densities at specific overpotentials with increasing nickel content suggest that all the nickel nanoparticles incorporated into GA structure is electrocatalytically active.

Tafel plots are quite useful in assessment of reaction kinetics by comparing overpotentials and current densities. Figure 5-17b presents Tafel plots of Ni/GA samples and the corresponding Tafel slopes are tabulated in Table 5-4. With increase in metal loading, the Tafel slopes decreased steadily reaching 61 mV dec⁻¹ for Ni/GA_{0.4}. The pioneering work on electrocatalytic mechanisms of OER on nickel surfaces is conducted by Juodkasis et al [225]. Accordingly, Tafel slopes of 60 mV dec⁻¹ is observed when the rate-determining step is the reaction presented in Equation (5-13). [225] Turnover frequency (TOF) of a catalyst is another valuable parameter that assesses the quality. Specifically, TOF is an expression of rate of O₂ molecules evolved per metal atom for OER. [226] and it can be calculated with the following equation:

$$TOF (s^{-1}) = \frac{jA}{4Fn} \quad (5-16)$$

where *j* is the current density (in A cm⁻²) at a specific overpotential, *A* is the geometric area of the electrode (in cm²), *F* is Faraday constant (96485 C mol⁻¹), *n* is the number of moles of the catalyst). There are two common ways to calculate TOF value: first one is taking all nickel atoms into account in the catalyst by means of mass loading, the other is calculated considering only number of nickel atoms on the surface which can be deduced from the ratio of fraction of nickel atoms to the overall surface area. [227] The former is known as the lower limit, TOF_{min}, and the latter is the upper limit, TOF_{max}. Generally, it is impossible to calculate the surface nickel atoms and TOF_{min} is reported. Here we report TOF_{min} values, assuming all the nickel atoms present in the structure is catalytically active.

Table 5-4 tabulates TOF values of Ni/GA electrocatalysts calculated at η of 350 mV. Highest TOF is obtained with Ni/GA_{0.4}, which is 3-fold higher than that of Ni(OH)₂ nanospheres reported in the literature and 10-fold higher than that of IrO₂ nanoparticles (Table 5-5). In fact, all the Ni/GA samples exhibited higher TOF values than those reported in the literature indicating superior activity of our catalysts.

Table 5-4 Electrochemical properties of Ni/GA with different Ni loadings

Sample	Onset potential / V	η at 10 mA cm^{-2} / mV	η at 10 mA cm^{-2} / mV (after stability test)	J at $\eta=350$ mV/ mA cm^{-2}	Tafel slope / mV dec^{-1}	TOF / s^{-1}
Ni/GA _{0.01}	2.33	1150	-	0.6	-	-
Ni/GA _{0.05}	1.61	480	530	0.71	76	0.03
Ni/GA _{0.1}	1.59	410	420	2.33	71	0.04
Ni/GA _{0.2}	1.55	370	390	6.77	69	0.06
Ni/GA _{0.4}	1.54	320	320	21.0	61	0.11

Apart from the high performance, stability is a critical issue in determination of the overall performance. For that purpose, chronopotentiometric measurements were conducted at 10 mA cm^{-2} for 2 h. Figure 5-17b presents the corresponding stability curves. The low activities of Ni/GA_{0.05} and Ni/GA_{0.1} are also reflected in stability test where η increased steadily in 2 h. Conversely, Ni/GA_{0.2} and Ni/GA_{0.4} sustained the η -value constant during 2 h of measurement. Furthermore, Figure 5-18 compares OER polarization curves of all the samples before and after the stability tests and tabulates the corresponding overpotential values at 10 mA cm^{-2} . The

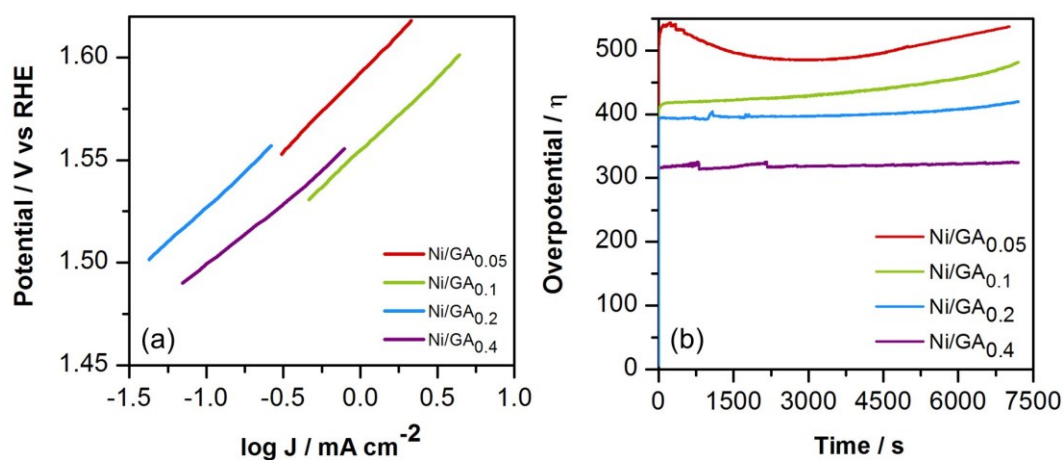


Figure 5-17 (a) Tafel plots of Ni/GA samples (b) Chronopotentiometric stability tests of Ni/GA samples at 10 mA cm^{-2} for 2 h

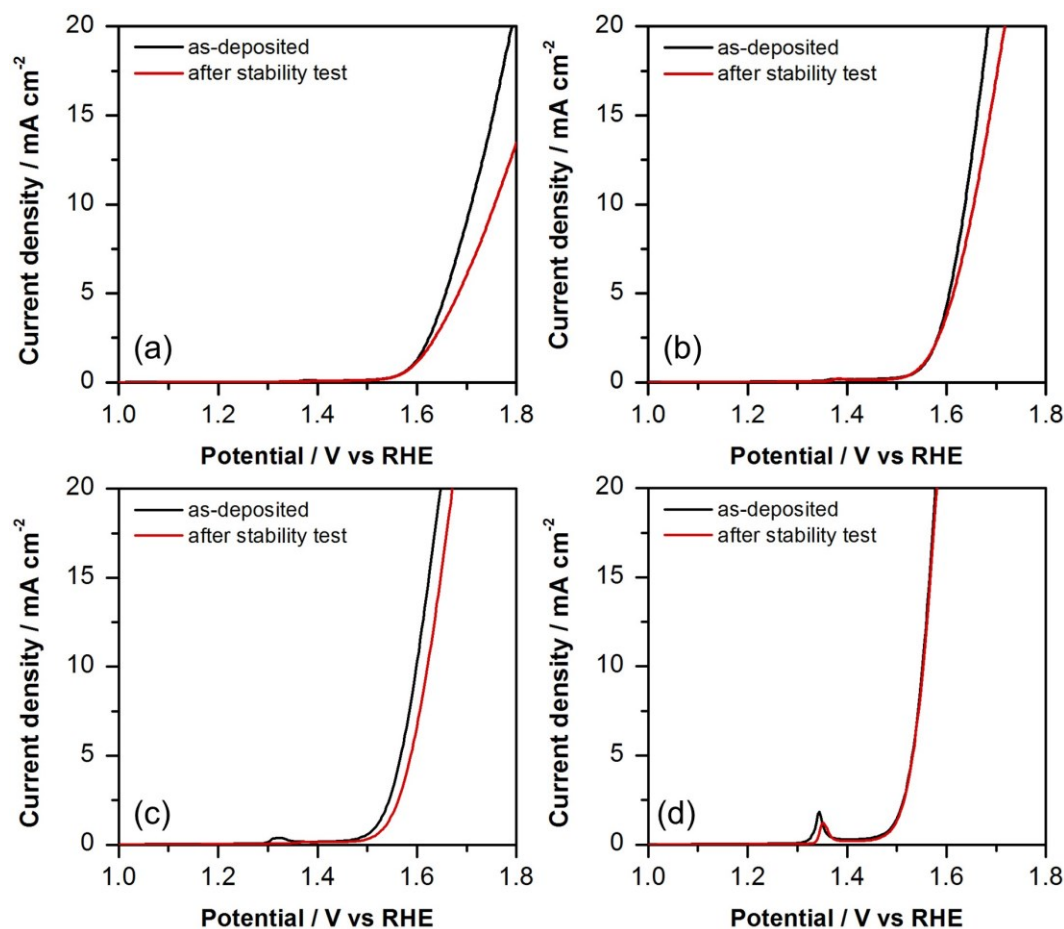


Figure 5-18 OER polarization curves of (a) Ni/GA_{0.05} (b) Ni/GA_{0.1} (c) Ni/GA_{0.2} (d) Ni/GA_{0.4} in O₂-saturated 1 M KOH at 10 mV s⁻¹ and 1600 rpm before and after the stability tests at 10 mA cm⁻² for 2 h

polarization curves changed a little, and the overpotentials shifted slightly (10 mV towards more positive potentials, 50 mV for Ni/GA_{0.05}). The polarization curve of Ni/GA_{0.4} did not change at all after 2 h of chronopotentiometric measurement.

Overall, Ni/GAs with Ni contents equal or higher than 20 wt% exhibited excellent OER performance, in agreement with VB spectroscopy results. The metallic character of Ni/GA_{0.2} and Ni/GA_{0.4} were found to be the highest, which can be beneficial for the fast electron transfer during the rate-determining steps of the overall reaction. Conversely, the electronic structure of Ni/GA_{0.01} and Ni/GA_{0.05} were proved to be governed by rGO solely, which is apparently not sufficient to exploit the activity the metal nanoparticles. Ni/GA_{0.1} exhibited activity and stability in an

intermediate-level, the loading (~ 10 wt%) was probably not high enough to obtain sufficiently low overpotentials and high current densities.

Table 5-5 Comparison of electrocatalytic activity of Ni-based OER catalysts reported in the literature

Material	Electrolyte	Onset potential / V	η at 10 mA cm^{-2} / mV	Tafel slope / mV dec^{-1}	TOF / s^{-1}	Catalyst loading / wt%	Reference
Ni/GA	0.1 M KOH	NA	430	132	NA	24.8	[217]
Ni@few-layer graphene	1.0 M KOH	1.45	280	45	NA	74.6	[228]
α -Ni(OH) ₂	0.1 M KOH	1.54	331	42	0.0361	100	[229]
Ni@graphene	1.0 M KOH	1.53	370	66	NA	74.1	[212]
NiO/MWCN T	0.5 M KOH	NA	409	120	NA	~ 33.3 (NiO)	[230]
Ni@N-graphene	0.1 M KOH	NA	320	189	NA	52.3	[231]
NiO/carbon cloth	0.1 M KOH	1.52	422	116	NA	NA	[208]
NiO/CNT	1.0 M KOH	1.52	410	40	NA	12.5 (NiO _x)	[210]
Ni(OH) ₂ /MWCNT	0.1 M KOH	1.55	474	87	0.015	39.4 (Ni(OH) ₂)	[209]
NiO _x	1.0 M NaOH	NA	420	NA	NA	100	[226]
Ir/C	0.1 M KOH	NA	380	NA	NA	20.0	[206]
Ru/C	0.1 M KOH	NA	390	NA	NA	20.0	[206]
IrO ₂	1.0 M KOH	1.52	338	47	0.01	100	[204]
Ni/GA _{0.2}	1.0 M KOH	1.55	370	69	0.06	22.6	This work
Ni/GA _{0.4}	1.0 M KOH	1.54	320	61	0.11	40.0	This work

5.4. Conclusions

In this chapter, graphene aerogels were decorated with nickel nanoparticles via one-step hydrothermal reaction followed by thermal reduction. For the optimal reaction conditions, different additives were used in the hydrothermal reaction medium along with Ni²⁺ source. The

additives used were urea, thiourea, acetamide, L-cystine, L-threonine, L-alanine, and glycine. Preliminary results showed that addition of urea, thiourea, glycine, L-cystine, and L-threonine produce monolithic hydrogels. TGA results showed that the highest nickel content can be achieved by addition of urea and L-cystine. These samples were further thermally reduced to form nickel nanoparticles. While Ni/GA produced from urea resulted in nicely dispersed small nanoparticles, those produced with L-cystine had microscopic sulfur compounds along with the nanoparticles which can be detrimental to the catalytic activity.

Ni/GAs synthesized with addition of urea were systematically analyzed as OER electrocatalysts. By tuning the Ni:GO ratio in the initial hydrothermal reaction, Ni content was varied from 1.5 to 40 wt% in a highly-controlled fashion. Thermal reduction for the formation of nickel nanoparticles resulted in further deoxygenation of GA structure simultaneously. The size of nickel nanoparticles was around 5-10 nm, regardless of loading. While Ni/GA_{0.01} showed no electrocatalytic activity towards OER, higher nickel loadings enhanced the electrocatalytic activity towards OER gradually. Based on the overpotentials required at 10 mA cm⁻², the electrocatalytic activity followed the order: Ni/GA_{0.4}>Ni/GA_{0.2}>Ni/GA_{0.1}>Ni/GA_{0.05}. In fact, Ni/GA_{0.4}, exhibited small overpotential of 320 mV at 10 mA cm⁻² with a high TOF value (0.11 s⁻¹), outperforming commercial catalysts like Ru/C and Ir/C. In the chronopotentiometric measurements, Ni/GA_{0.2} and Ni/GA_{0.4} exhibited excellent stability whereas poorer performance was observed with Ni/GA_{0.05} and Ni/GA_{0.1}.

Chapter 6: Graphene Aerogels Supported Pt Nanoparticles as Electrocatalysts for Oxygen Reduction Reaction

This chapter includes a collaborative work between research groups of Assoc. Prof. Dr. Uğur Ünal, Prof. Dr. Can Erkey of Chemical and Biological Engineering Department, Koç University, and Prof. Dr. Mark Aindow of Material Science and Engineering Department, University of Connecticut. The results of this chapter is published as a full-paper in *Electrochimica Acta* in 2017. [214]

6.1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are attractive devices due to their simplicity, high power density, low operating temperature, and quick start-up. [232] The slow kinetics of the oxygen reduction reaction (ORR) are well known, and Pt has been the catalyst of choice to accelerate the reaction rate. [64] High Pt loadings are often necessary to reach the desired power densities. Thus, minimizing the Pt loading while enhancing its catalytic activity towards the ORR is of both academic and industrial interest.

Support materials for ORR catalysts should possess high surface area and appropriate porosity to enhance dispersion of metal particles and diffusion of reactants and products. Generally, carbonaceous materials are used as support materials due to their intrinsic electrical conductivity, chemical inertness, and high surface area. [64] The microstructure of the carbon support is a crucial parameter affecting the electrocatalytic activity of the Pt directly. [233] Especially, mesoporous carbons have been found to result in higher catalytic activities than commercially used carbon black. These mesoporous supports enhance the interaction between the reactants and the catalyst and the electrolyte by allowing penetration of Nafion, and also promote diffusion of the reactants and removal of the products to and from the active sites in the three phase interface. [234,235]

Graphene comprises a two-dimensional sp^2 -hybridized carbon network, which exhibits excellent electrical and thermal conductivity, high mechanical strength, and high theoretical surface area.

[2] In particular, graphene aerogels (GAs) are a fascinating class of materials combining the favorable properties of graphene with the high porosity and low density of aerogels. [236] In this regard, mesoporous GAs with high conductivity are potential candidates as support materials for ORR catalysts. There are a few reports on the electrochemical activities of Pt nanoparticles deposited onto GAs by hydrothermal [237] and solvothermal [238] techniques. Zhao *et al.* reported that GA-supported Pt particles showed a higher catalytic activity for methanol electrooxidation than 2D graphene supported Pt; the higher performance was attributed to the 3D porous structure of GA. [238]

Supercritical deposition (SCD) is an emerging technique that is used to prepare supported nanoparticles. SCD consists of the dissolution of a metal precursor in the supercritical fluid followed by the adsorption of the precursor onto the support. Subsequent conversion of the precursor to the corresponding metal or metal oxide can be achieved by *in situ* or *ex situ* routes. [239,240,249,250,241–248] SCD on carbon, resorcinol formaldehyde and silica aerogels usually results in highly dispersed Pt nanoparticles with very narrow particle size distributions on the interior surfaces of the aerogel particles. [251] Moreover, SCD is a suitable method for preparation of supported nanoparticles on aerogels without disrupting the nanostructure, which is otherwise prone to collapse due to the capillary pressures occurring during the conventional drying of the impregnation solvent. Various electrocatalysts produced via the SCD technique have exhibited promising catalytic properties and have outperformed commercial catalysts. [252,253] Bayrakceken *et al.* [252] compared the electrocatalytic activity of a Pt/VXR catalyst prepared by SCD to that of a commercial ETEK Pt/VXR prepared by wet impregnation (10 wt% Pt); the electrochemical surface area (ESA) of the catalyst prepared by SCD was about three times larger than that of the ETEK catalyst. Ang *et al.* [254] reported a comparison of Pt/C catalysts prepared by wet impregnation and SCD techniques in terms of their stability in the ORR. The Pt/C catalyst

prepared via SCD was shown to be much more durable after electrochemical cycling; the Pt particles remained highly dispersed during the stability tests whereas the ones prepared via wet impregnation agglomerated heavily. Graphene sheet supported Pt catalysts prepared via the SCD route had higher catalytic activity than Pt/carbon black (Vulcan XC-72) [255], Pt/MWCNT, and commercial Pt/C [256] towards methanol electrooxidation.

This chapter includes SCD of Pt nanoparticles onto graphene aerogels and their use as electrocatalysts for the ORR. The GA support was synthesized via a one-pot hydrothermal self-assembly route without any surfactants, binders, or reducing agents. Highly dispersed Pt nanoparticles could be deposited onto the 3D porous GA network in a highly controlled fashion via the SCD technique. By altering the precursor conversion temperature, the Pt nanoparticle sizes and distributions could easily be controlled. Samples were characterized using N₂ adsorption, Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The effect of the precursor conversion temperature on the electrocatalytic activity of the Pt/GAs in the ORR was investigated using CV and RDE.

6.2. Materials and Methods

6.2.1. Materials

All the chemicals were used as received without further purification. Graphite (natural, -200 mesh, 99.9995%) and NaNO₃ (99%) were purchased from Alfa Aesar. KMnO₄ and H₂O₂ (30%) were obtained from Merck Millipore. HCl (37%), H₂SO₄ (95-97%) were obtained from Sigma Aldrich. Dimethyl(1,5-cyclooctadiene)platinum(II) (Pt(cod)me₂, 99%, MW=333.33 g mol⁻¹) was purchased from STREM Chemicals, Inc. Carbon dioxide, nitrogen and oxygen were all at 99.998% purity. Water was distilled and deionized before usage.

6.2.2. Synthesis of Graphene Aerogel (GA)

GA was prepared with the procedure explained in Section 4.2.2.

6.2.3. Preparation of Pt/GA Nanocomposites via SCD

Adsorption of Pt precursors on GA was performed in Energy Technologies and Supercritical Fluids Research Group of Prof. Can Erkey in Koç University. Predetermined amounts of GA and Pt(cod)me₂ were placed in a custom-made high pressure stainless steel vessel equipped with two sapphire windows (57 mL internal volume) along with a magnetic stirrer to ensure complete mixing of the precursor and scCO₂. A syringe pump (ISCO Model 260D) was used to pressurize the CO₂ to the desired level, and the temperature was kept constant during all experiments with the help of a circulator heater (Fischer). All deposition experiments were conducted at 35 °C and 10.7 MPa. After thermodynamic equilibrium was reached, the vessel was depressurized slowly (0.7 MPa min⁻¹), and the Pt(cod)me₂/GA composites were then taken out of the vessel.

6.2.4. Precursor Conversion

Pt precursor conversion into Pt nanoparticles was performed in Energy Technologies and Supercritical Fluids Research Group of Prof. Can Erkey in Koç University. The conversion of the Pt(cod)me₂/GA nanocomposites was carried out thermally at ambient pressure under flowing N₂ (100 mL min⁻¹). The prepared nanocomposites were placed in a quartz tube (220 mm internal diameter, 4 mm wall thickness and 610 mm length) in a tube furnace (Thermolyne model F1125) and heated to 200, 400, 600 and 800 °C (named thereafter Pt/GA(200), Pt/GA(400), Pt/GA(600), and Pt/GA(800)) with a temperature ramp of 20 °C min⁻¹ and kept at that temperature for 4 h. The nanocomposites were removed from the tube furnace upon cooling.

6.2.5. Structural Characterization

The pore size, pore volume and Brauner, Emmet and Teller (BET) surface area of samples were determined via nitrogen physisorption using a Micromeritics ASAP 2020 instrument. N₂ adsorption/desorption isotherms with a relative pressure (P/P₀) ranging from 10⁻⁷ to 0.999 were obtained. The pore size distributions of samples were determined through the Barret, Joyner and Halenda (BJH) method. Pore sizes were determined from the desorption isotherm due its

thermodynamic stability. Values of micropore volume and area were obtained using the t-plot method. The crystal structure of the samples were determined using XRD (Bruker D8, Advance) with a Cu K α source. Pt particle sizes were determined from the broadening of (220) peak for face-centered cubic (FCC) Pt using the Scherrer equation. A low background Silicon sample holder was used for all XRD measurements. Raman measurements were conducted with Raman microscope (Renishaw inVia) using an excitation wavelength of 532 nm and a 50x objective. The spectra from the samples were corrected with respect to Silicon peak at 520 cm⁻¹. For each sample, three separate measurements were taken to ensure reproducibility. All spectra were recorded between 200-3500 cm⁻¹ for 20 seconds. To avoid local heating and damaging of the samples, the laser power was set to 5 mW. Fitting of Raman spectra was conducted with Fityk software. The Pt loadings of the samples were determined using thermogravimetric analysis (TGA, TA Instruments TGA Q500). Samples were heated to 500 °C under flowing air at a ramp rate of 10 °C/min and a flowrate of 100 mL/min. For the evaluation of functional groups of GA with thermal treatment, TGA was conducted under N₂ flow. XPS measurements were conducted using a Thermo K-Alpha Spectrometer with an Al K α source. The fittings for the experimental data were done with Advantage software. For quantification of relative intensities (with respect to the C-C/C=C/C-H peak) of carbon functional groups, the C 1s region spectra were used. C/(C+O) ratios were determined from atomic percentages (calculated from overall fitted areas) of C 1s and O 1s region spectra. The morphologies of the samples were characterized by high resolution TEM and scanning TEM (STEM) in University of Connecticut. Specimens were prepared by carefully crushing the Pt/GA samples using a mortar and a pestle set. Distilled water was then added to resulting powders and sonicated to create a uniform suspension. A Quantifoil 200 mesh copper grid coated with a holey carbon film was immersed in the suspension and removed with a droplet of suspension on the grid surface. The solvent was allowed to evaporate in air and then kept in a vacuum desiccator overnight to remove any residual moisture. High resolution phase contrast TEM images and high-angle annular dark-field (HAADF) STEM images were acquired using a

JEOL 2010 FasTEM and an FEI Talos F200X S/TEM, respectively. Both instruments were operated at an accelerating voltage of 200 kV. Particle size distributions were obtained from HAADF STEM images by measuring 200 nanoparticles and plotting histograms binned in 0.5 nm increments. STEM X-ray maps were also obtained in the FEI Talos F200X, which is equipped with a Super-X silicon drift detector (SDD) system that allows for rapid acquisition of energy-dispersive X-ray spectroscopy (EDXS) data. The Pt X-ray maps correspond to the integrated EDXS intensities in the Pt L peaks.

6.2.6. Electrochemical Characterization

Electrochemical tests were performed in Energy Technologies and Supercritical Fluids Research Group of Prof. Can Erkey in Koç University. CV was utilized for the electrochemical characterization of the samples using a three-electrode electrochemical cell connected to a potentiostat (Pine Instrument Company Model AFCBP1). A glassy carbon disk (internal diameter 0.196 cm²) was used as the working electrode (Pine Instruments), Ag/AgCl filled with saturated KCl solution (Gamry Instruments) was used as the reference electrode, and a Pt wire was utilized as the counter electrode. The electrolyte was a 0.1 M HClO₄ solution. A catalyst ink was prepared by mixing a certain amount of catalyst with 1,2-propandiol, distilled water and 5 wt% Nafion solution (Ion Solutions Inc.). The Pt loading on the electrode was 28 µg cm⁻². The suspension was achieved using an ultrasonic water bath (Ultra-Turrax® T25) for 30 min prior to deposition. 5.8 µL of the ink was deposited onto the glassy carbon disk and left to dry at ambient temperature and pressure overnight. The electrolyte was purged for 30 min with N₂ prior to electrochemical analysis to remove any O₂. Then, the N₂ supply line was removed from the solution and placed just above the electrolyte to provide a N₂ blanket during analysis. All CV experiments were conducted at room temperature. The CV curves were recorded between 0.05 and 1.2 V with respect to the normal hydrogen electrode (NHE) at a scan rate of 50 mV s⁻¹. RDE experiments were conducted in the same electrochemical cell by saturating the electrolyte solution with O₂ for 30 min prior to

analysis. Five different rotation speeds (100-2500 rpm) were employed with a scan rate of 10 mV s⁻¹. The ORR curves were recorded between 0.1 and 1.0 V with respect to NHE.

6.3. Results & Discussion

6.3.1. Structural Properties of Pt/GA Nanocomposites

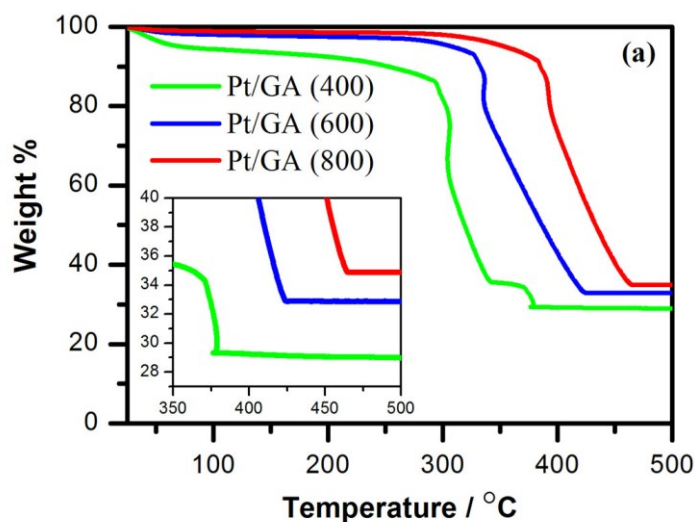


Figure 6-1 TGA curves of Pt deposited samples in air. Flow rate: 100 mL min⁻¹

Table 6-1 Pt Loading of Pt/GA samples determined via TGA

Sample	Pt Loading (wt.%)
Pt/GA(400)	28.9
Pt/GA(600)	32.9
Pt/GA(800)	34.9

Pt/GA nanocomposites were prepared by adsorbing Pt(cod)me₂ in scCO₂ at 35 °C and 10.7 MPa on GA. Once the adsorption equilibrium was reached, the vessel was depressurized, and the adsorbed Pt(cod)me₂ was converted thermally to Pt at ambient pressure. Table 6-1 shows the overall Pt loadings of the Pt/GA samples after thermal conversion under ambient pressure at different temperatures (TGA curves in Figure 6-1). The metal loadings of the Pt/GA samples are close to each other. The slight increase in Pt loading is presumably the result of a loss of functional

groups of GA with increasing conversion temperature, so that the relative amount of Pt on GA increases.

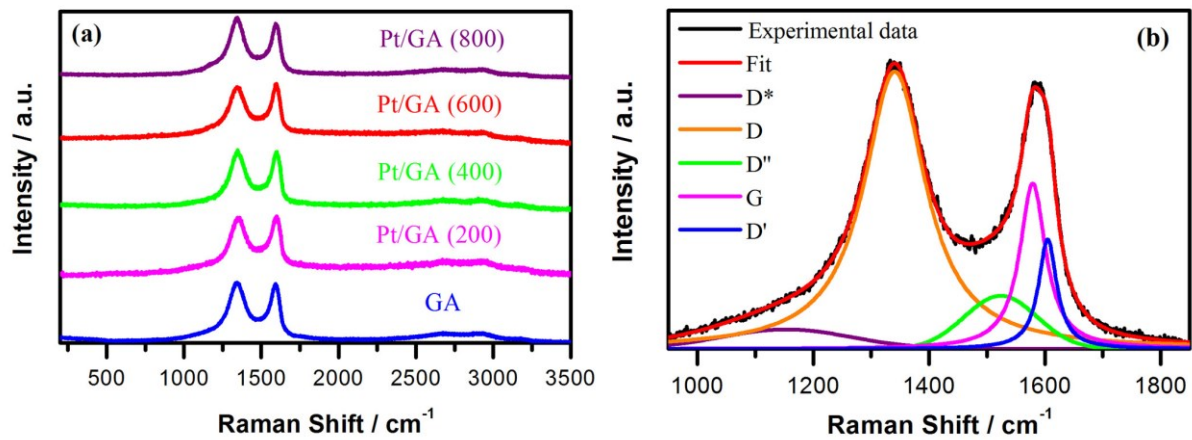


Figure 6-2 Raman spectra of GA and Pt deposited GAs converted at different temperatures (a), exemplary five peak deconvolution for GA (b)

Figure 6-2a shows Raman spectra of as-synthesized GA and Pt deposited aerogels. All spectra exhibit bands typical of disordered graphene. For the quantification of defects, we have deconvoluted the region in 1000-1800 cm⁻¹ into three Lorentzian (D, G, and D') and two Gaussian peaks (D* and D'') (Figure 6-2b, Figure 6-3). Table 6-2 shows the corresponding peak positions and relative ratios. In Pt deposited samples, the D and G bands red-shifted and the I_D/I_G ratio increased as the conversion temperature increased. The red-shift in the D and G bands indicates the reduction of graphene aerogel with thermal treatment in accordance with the TGA results. [18] The increase in I_D/I_G ratio signifies an increase in the amount of defects in the structure and a decrease in the average sp² crystallite size. [87] Moreover, the D* band is related to the disordered graphitic lattice in the structure, and the D'' band is related to amorphous phases. [86] Both I_{D^*}/I_G and $I_{D''}/I_G$ ratios decreased until conversion temperature of 400 °C, then both started to increase. Decreases in both I_{D^*}/I_G and $I_{D''}/I_G$ ratios are expected up to 400 °C due to deoxygenation of the GA. The increase above 400 °C may be related to growth of the Pt nanoparticles and consequently, distortion of the graphitic lattice and the crystal structure. Furthermore, the D' band is the disorder-induced phonon mode arising from crystal defects. With the increase in the conversion

temperature of the Pt-deposited GAs, the increase in the $I_{D'}/I_G$ ratio indicates the formation of further vacancies, pentagon/heptagon defects, and reconstructed zigzag (5-7) defects. [198]

Table 6-2 Relative peak intensities and peak positions calculated from fitted Raman spectra.

Sample	I_D/I_G	I_{D^*}/I_G	$I_{D''}/I_G$	$I_{D'}/I_G$	D (cm^{-1})	G (cm^{-1})
Pt/GA(200)	1.29	0.07	0.25	0.33	1348	1589
Pt/GA(400)	1.36	0.05	0.24	0.54	1347	1588
Pt/GA(600)	1.48	0.09	0.28	0.67	1343	1585
Pt/GA(800)	1.90	0.15	0.39	0.81	1341	1583

D*: associated with the disordered graphitic lattice

D: A_{1g} breathing mode of sp^2 hybridized carbon

D'': associated with the amorphous phases

G: E_{2g} mode of sp^2 hybridized carbon

D': disorder induced phonon mode

Figure 6-4a shows the XRD patterns of as-synthesized GA and Pt/GA nanocomposites converted at different temperatures. In the XRD data from GAs, the peak around $2\theta = 24^\circ$ belongs to (002) peak of graphite which is typically observed in reduced graphene oxides. [157] The interlayer distance (d_{002}) of this peak is calculated as 0.371 nm using Bragg's law. The (002) peak is also observable in Pt deposited aerogels and it shifts to higher 2θ values with increasing conversion temperature as shown in Figure 6-4b. This corresponds to a decreasing interlayer spacing for the (002) plane due to the deoxygenation of graphene oxide with increasing temperature, in agreement with Raman and TGA data. The second peak in the XRD pattern of GA is assigned to (100) of graphite. [257] The XRD from the Pt/GA samples, except for Pt/GA(200), exhibited the four main peaks ((111), (200), (220) and (311)) of FCC Pt, showing that Pt was in its metallic form in all samples. The XRD data from Pt/GA(200) show very broad and weak peaks suggesting incomplete transformation of the Pt precursor into the metallic form. Moreover, all of the Pt diffraction peaks became sharper with increasing conversion temperatures, indicating that the Pt

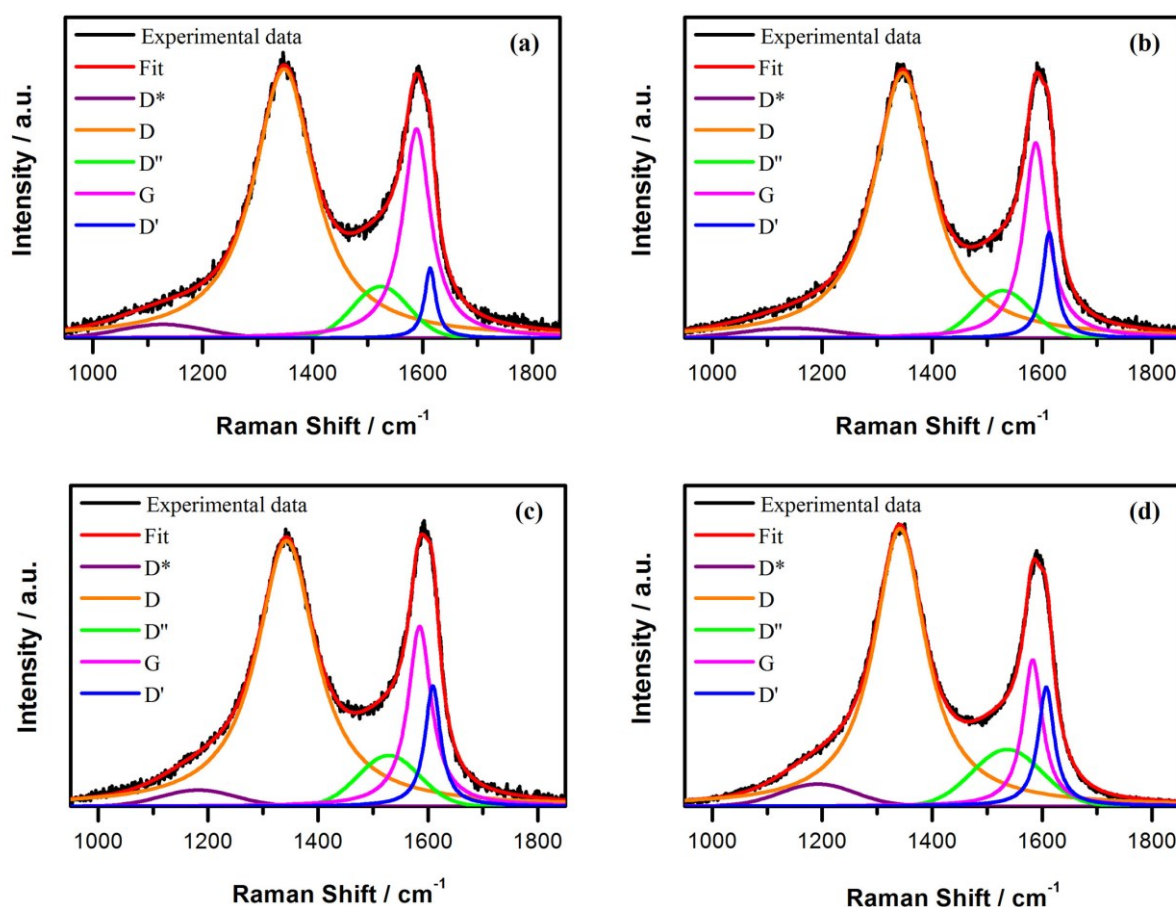


Figure 6-3 Fitted Raman spectra of (a) Pt/GA(200) (b) Pt/GA(400) (c) Pt/GA(600) (d) Pt/GA(800)

particles coarsen. The average Pt particle size was determined from the (220) peak width using the Scherrer equation. The increase in the average Pt particle size upon heating from 400 °C to 600 °C is less significant (1.2 and 1.7 nm, respectively) than the increase upon heating from 600 °C to 800 °C (1.7 and 2.9 nm, respectively). Furthermore, the XRD of Pt/GA(800) revealed the bimodal Pt particle size distribution in this sample where a fraction of the Pt nanoparticles were fitted to have an average size of 2.9 nm while another fraction had an average size of 23 nm.

XPS was utilized to quantify the changes in functional groups of GA with conversion temperature. XPS C 1s spectra of all samples (Figure 6-5a) can be deconvoluted to five peaks, each belonging to various functional groups present in the GA structure. The peaks around 284.5, 285.4, 286.5, 288.6, and 290.7 eV correspond to carbon-carbon/carbon-hydrogen (C-C/C=C/C-H), alkoxy

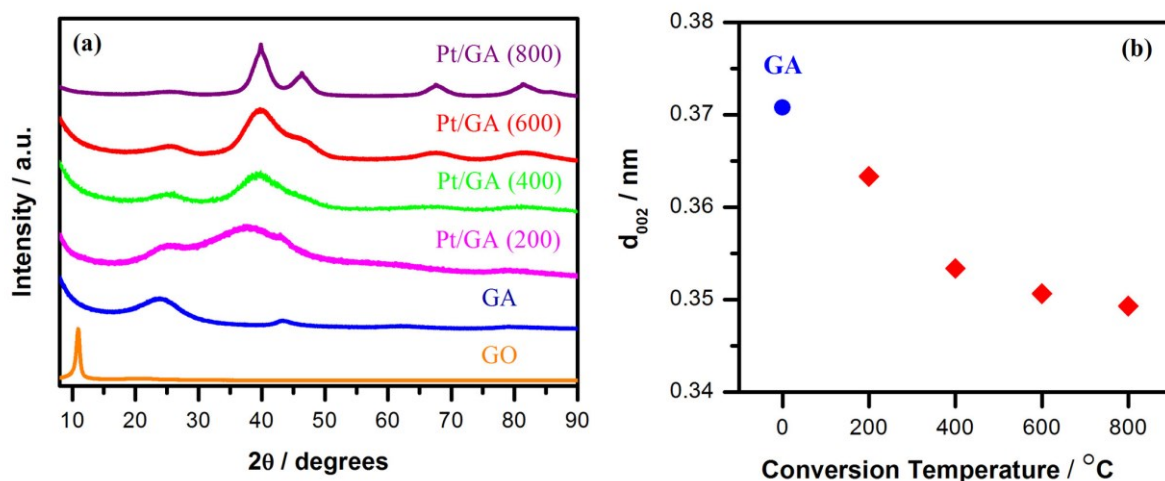


Figure 6-4 (a) XRD diagrams of GO, GA and Pt deposited GAs converted at different temperatures, (b) Interlayer distance of (002) plane of Pt/GA vs conversion temperature (● shows the d_{002} value for as-synthesized GA).

(C-OH), epoxy (C-O-C), double bonded carbon in carbonyl (C=O) and carboxyl (HO-C=O) groups, and $\pi - \pi^*$ shake-up satellites, respectively. [16,84,195] Figure 6-5b shows the relative intensity change (with respect to C-C/C=C/C-H peak) of the functional groups with change in conversion temperature for the Pt deposited samples. Compared to the GA, the relative intensities of the C-OH and C-O-C groups decreased sharply, even at 200 °C. From 200 to 800 °C, the C-O-C and C=O intensities declined continuously, which shows the efficient reduction of these groups with thermal treatment. Interestingly, the intensity of the C-OH peak first exhibited an increase up to 400 °C, then decreased gradually at higher conversion temperatures. Ganguly and Sharma *et al.* [84] addressed the anomalous thermal stability of the C-OH group during thermal treatment of graphene oxide; they ascribed this to the formation of new phenolic groups in the initial stages of thermal reduction, resulting in the observed rise in the intensity of the hydroxyl peak. Nonetheless, the total amount of functional groups in the GA structure decreased steadily with increase in conversion temperature (Figure 6-5c) in agreement with XRD and Raman results. Elemental analysis with XPS revealed that the total amount of carbon was 91.3 % (atomic) in the Pt/GA(800).

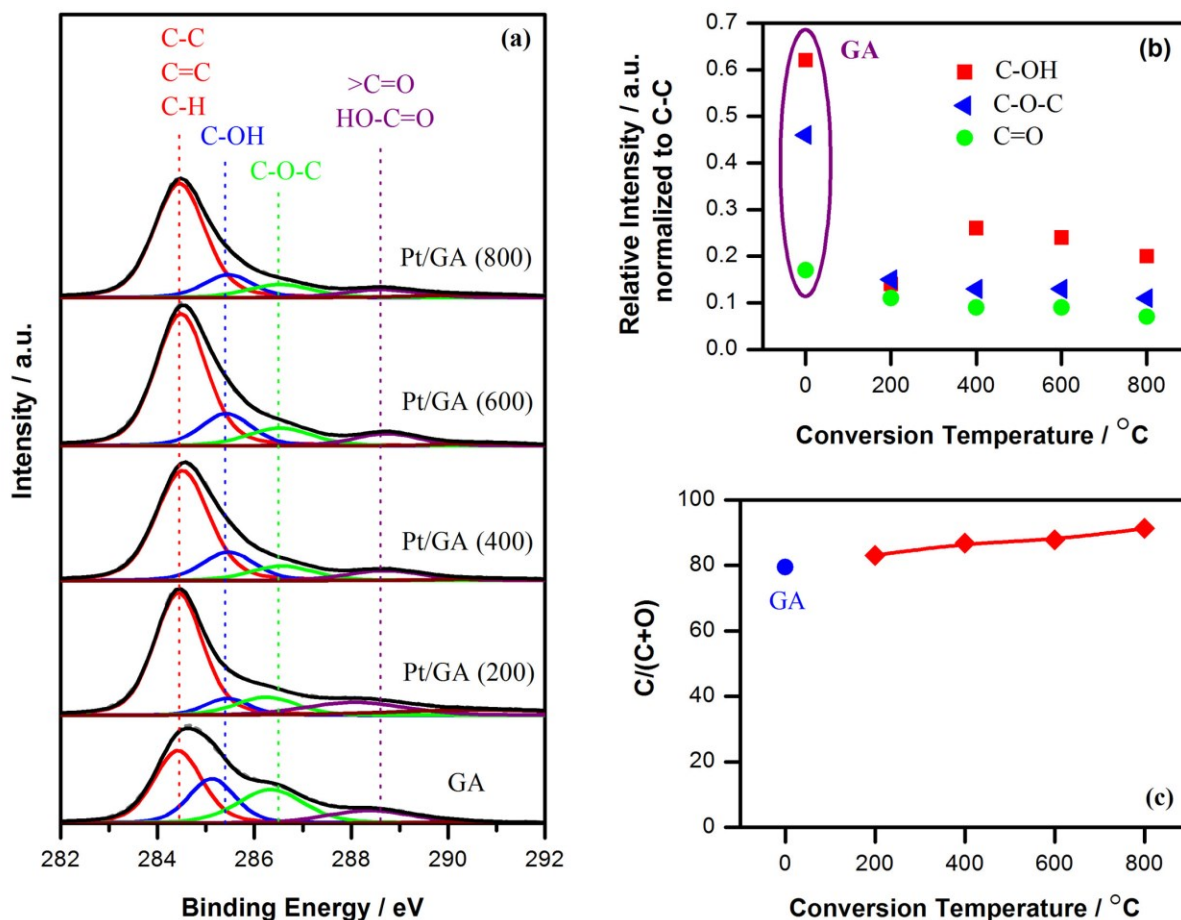


Figure 6-5 (a) XPS C 1s spectra of all samples. (b) Relative intensity of functional groups normalized to C-C peak intensity change with conversion temperature. (c) C/(C+O) (calculated from fitting C 1s and O 1s region spectra) vs conversion temperature.

Figure 6-6 shows the HRTEM images along with the Pt particle size distributions of Pt/GA samples converted at different temperatures. Here the light grey background and black dots represent the GA support and the Pt nanoparticles, respectively. The GA support was observed as wrinkled graphene sheets due to sample preparation procedure. The HRTEM images show homogeneously distributed Pt particles on the GA surfaces with very narrow particle size distributions for Pt/GA(400), Pt/GA(600) and Pt/GA(800). For the Pt/GA(800) sample, however, some larger Pt nanoparticles were observed, as shown in Figure 6-7. This is consistent with the Scherrer analysis of the XRD data from this sample. When similar or higher conversion temperatures were applied to prepare carbon aerogel (CA) supported Pt nanoparticles, no bimodal

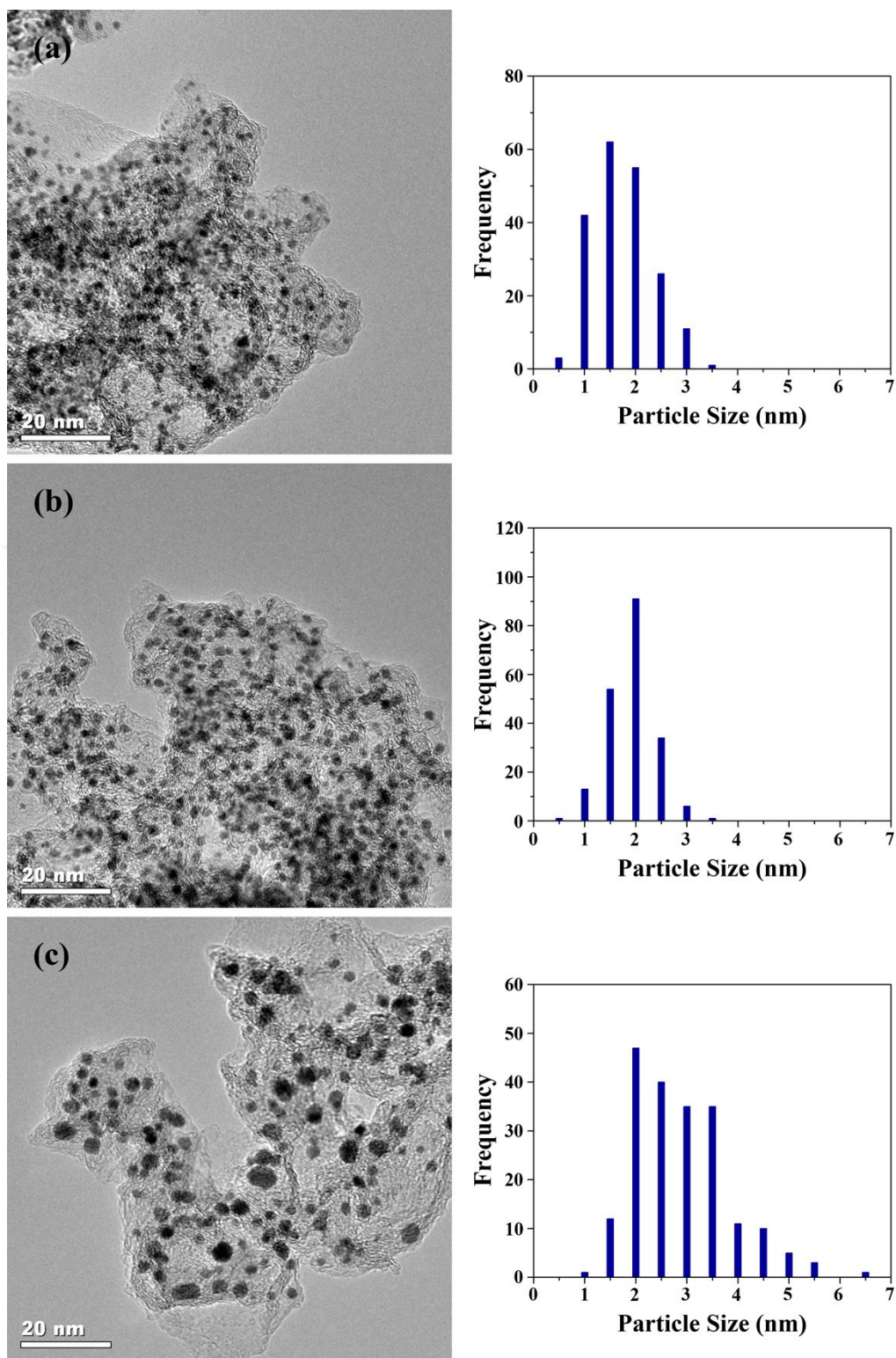


Figure 6-6 HRTEM images and Pt particle size distributions of Pt/GA(400), (b) Pt/GA(600), and (c) Pt/GA(800).

particle size distributions have been observed, regardless of the pore size of the support. [251] The presence of the larger particles on GA could thus be associated with the enhanced mobility of Pt on the individual 2D graphene sheets in the aerogel structure giving rise to easier particle growth

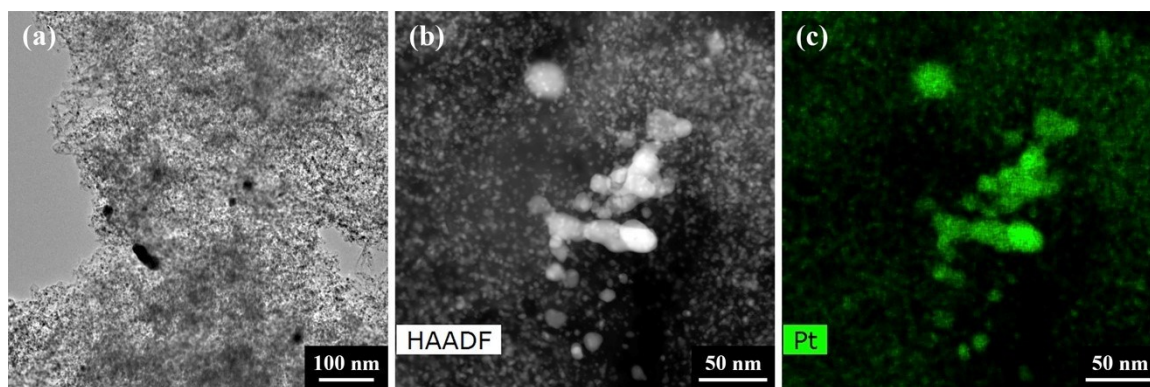


Figure 6-7 HRTEM, HAADF and EDXS images of large Pt nanoparticles present in Pt/GA(800).

at elevated conversion temperatures. Metal-support interaction, in the case of GA and Pt may be significantly weaker than CA and Pt, resulting in higher diffusion rates for smaller Pt nanoparticles adsorbed on the GA surfaces than for those on the pores at elevated conversion temperatures resulting significantly large Pt nanoparticles. The Pt nanoparticles adsorbed on the pores of the

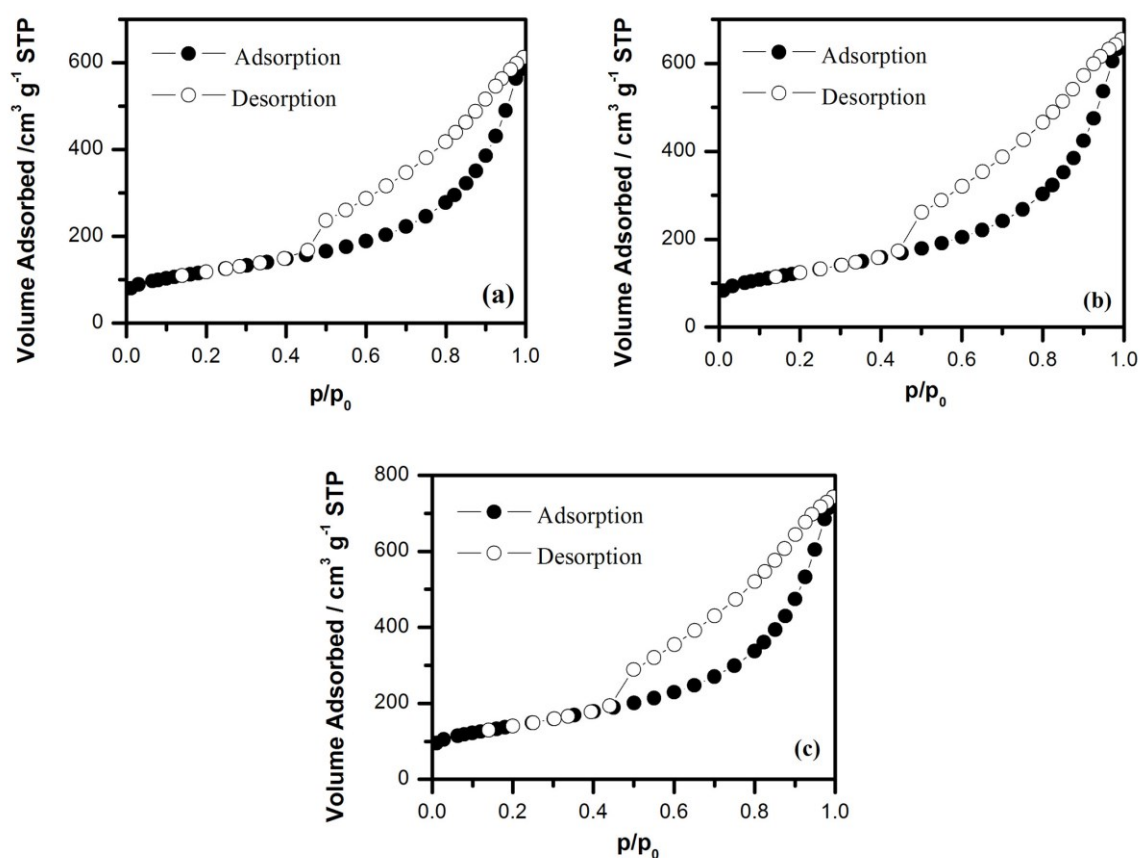


Figure 6-8 Nitrogen adsorption isotherms of (a) Pt/GA (400), (b) Pt/GA (600), and (c) Pt/GA (800).

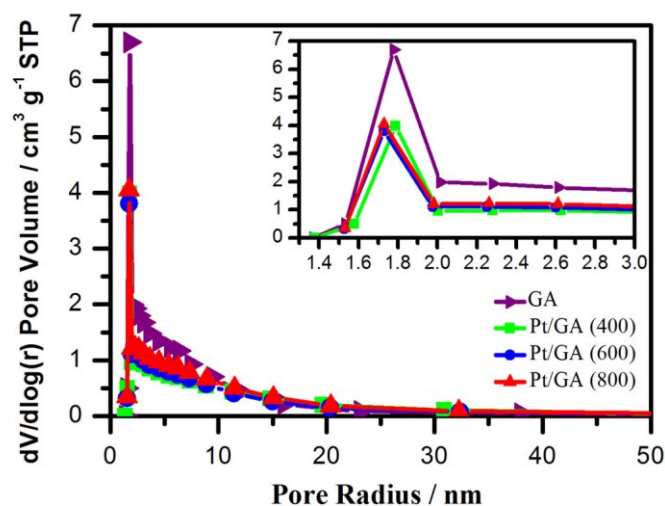


Figure 6-9 Pore size distributions of samples

GA, on the hand, are probably trapped inside the pores and cannot form Pt nanoparticles larger than the pore size of the GA (ca. 6 nm) regardless of the conversion temperature. However, the frequency of these large Pt nanoparticles is low, as the TEM images reveal. Moreover, the average Pt particle sizes obtained for the corresponding conversion temperatures for Pt/GAs were very close to those of Pt/CA prepared using SCD [251] showing that Pt particle size can be controlled with SCD followed by thermal treatment irrespective of the support employed.

Nitrogen adsorption isotherms of the Pt loaded samples (Figure 6-8) showed similar hysteresis loops to that of GA, indicating that the mesoporous structure was preserved. The surface areas of the Pt-loaded samples were smaller than that of the GA due to blockage of pores by Pt nanoparticles (Table 6-3). In the pore size distribution curves, there is a significant decrease in the pore volume of Pt/GA(400) compared to that of GA, especially in the micropore region (Figure 6-9). Also, when the conversion temperature is increased from 400 to 800 °C, a shift towards smaller pores in the micropore region is observed (inset of Figure 6-9) accompanied by a small increase in the pore volume of the mesopore region. Consequently, the total surface area and pore volume increased slightly with the increase in conversion temperature. This may result from the diffusion of Pt nanoparticles from micro to mesopores, and from further growth in those larger pores. [258]

Table 6-3 Pore properties of samples measured with Nitrogen adsorption.

Sample	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	Micropore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore diameter (nm)
GA	708	1.54	0.024	5.8
Pt/GA(400)	409	0.96	0.035	6.5
Pt/GA(600)	434	1.03	0.031	6.2
Pt/GA(800)	488	1.17	0.037	6.3

6.3.2. Electrochemical Properties of Pt/GA Nanocomposites

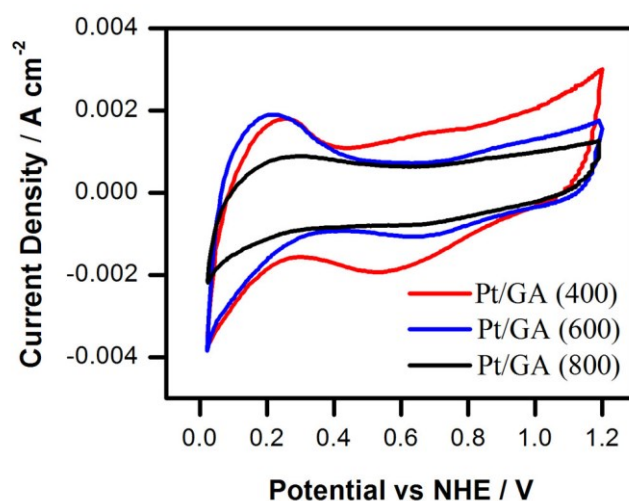


Figure 6-10 Cyclic voltammograms of Pt/GA samples taken in N_2 saturated 0.1 M HClO_4 electrolyte with a scan rate of 50 mV s^{-1}

The electrochemical behavior of the Pt/GA samples converted at different temperatures was determined through CV and RDE analyses. Figure 6-10 presents the cyclic voltammograms of the Pt/GA samples taken in N_2 -saturated acidic electrolyte. Since Pt/GA(200) showed incomplete formation of Pt particles in the XRD analysis, no electrochemical characterization was performed on this sample.

Figure 6-10 shows hydrogen adsorption/desorption peaks in the 0-0.3 V and Pt oxidation/reduction peaks in the 0.6-0.8 V range in both directions for all Pt/GA samples. The

hydrogen adsorption/desorption peak current densities of Pt/GA(400) and Pt/GA(600) are approximately the same and higher than that of Pt/GA(800) due to similar and smaller average Pt particle sizes of Pt/GA(400) and Pt/GA(600) (1.2 and 1.7 nm, respectively) when compared to Pt/GA(800) (2.9 nm). The ESA of the Pt/GA samples were calculated using the area under the hydrogen adsorption region by excluding the effect of capacitive current (Table 6-4).

Table 6-4 The average particle size and electrochemical properties of Pt/GA samples converted at different temperatures.

Sample	Particle Size (nm)		SA (m ² g ⁻¹) ^a	ESA (m ² g ⁻¹)	Pt Utilization (%)	Mass Activity (mA mg _{Pt} ⁻¹)	Specific Activity (μA cm ⁻²)
	XRD	TEM					
Pt/GA(400)	1.2	1.7 ± 0.6	234	71	30	27.2	6.6
Pt/GA(600)	1.7	1.9 ± 0.5	165	102	62	30.6	2.3
Pt/GA(800)	2.9	2.9 ± 0.9	85	43	51	12.0	34.4

^a SA=6*10³/Qd (Q_{Pt}=21.4 g cm⁻³, d:mean particle size)

Figure 6-11 presents the ORR curves of Pt/GA samples obtained by the RDE analysis in an acidic medium to simulate real PEMFC conditions. Mass and specific activities were determined by taking the kinetic current density at 0.85 V and 1600 rpm to rule out the effect of mass transfer limitations.

The ORR curves of the Pt/GA samples (Figure 6-11) followed an expected trend, namely increasing current densities with increasing rotation speeds at low voltages. Among the three samples, the Pt/GA(800) exhibited the lowest current densities in CV as a result of higher average Pt particle size. Furthermore, the ORR curves of this sample are more steep than those for Pt/GA(400) and Pt/GA(600), most likely due to lower ORR activity. Table 6-4 shows the measured electrochemical properties of the Pt/GA samples along with the average Pt particle sizes obtained from XRD and TEM.

Pt/GA(600) has the highest ESA of 102 m² g⁻¹, although this sample had a higher average Pt particle size (1.7 nm) than Pt/GA(400) (1.2 nm). This behavior may seem odd at first since one

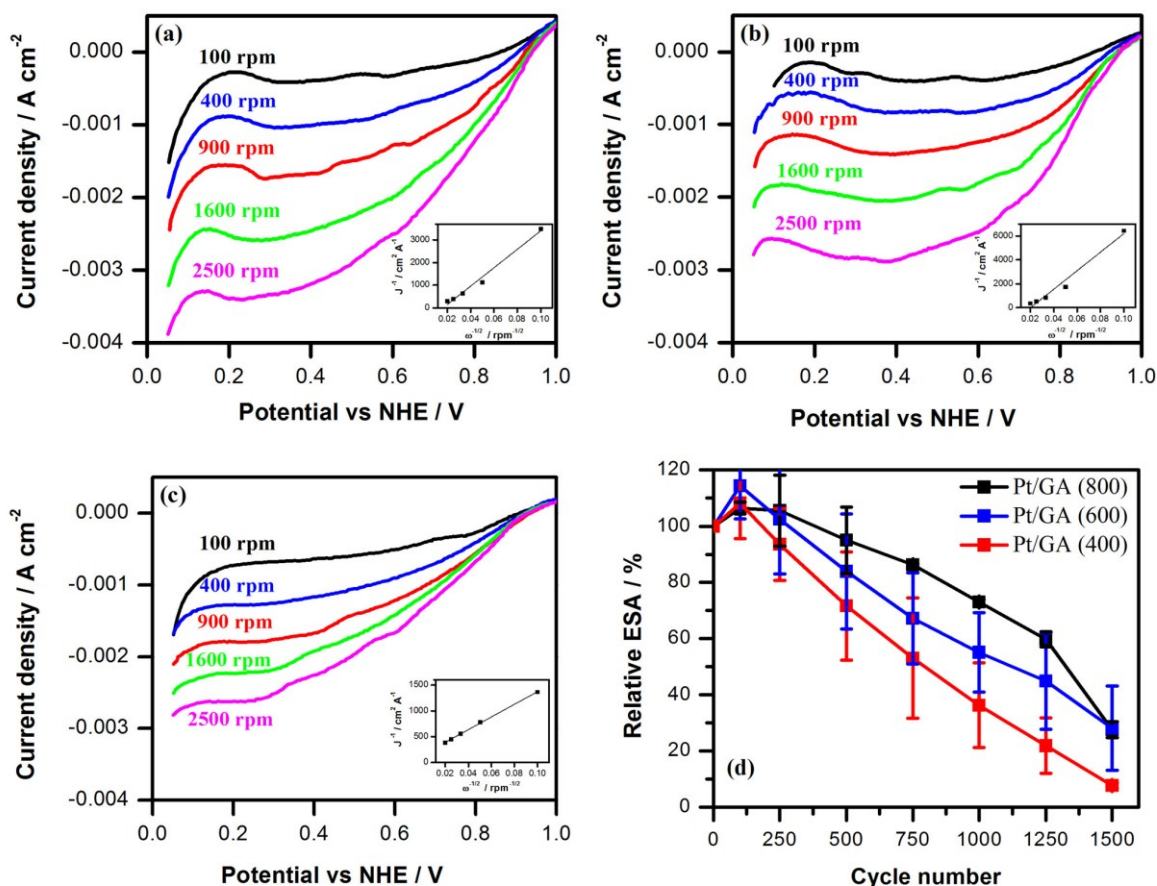


Figure 6-11 ORR curves of (a) Pt/GA(400), (b) Pt/GA(600), and (c) Pt/GA(800) taken in O₂ saturated 0.1 M HClO₄ electrolyte at five different rotation speeds (100-2500 rpm) with a scan rate of 10 mV s⁻¹. Koutecky-Levich plots are given as inset based on $1/j = 1/j_k + 1/B\omega^{1/2}$ calculated from 0.2 V vs NHE. (d) Relative ESA % (with respect to initial cycle) vs cycle number measured at scan rate of 50 mV s⁻¹. Error bars show standard deviations of averages.

would expect the ESA to increase with decreasing Pt particle size. This apparent discrepancy could be explained in the two following ways: (i) the oxygenated functional groups on the GA surface are still present after the conversion at 400 °C (as shown by XPS) and could easily bind to Pt active sites blocking H⁺ adsorption, and/or (ii) the significantly higher capacitive current density observed during the CV of Pt/GA(400) hinders the accurate calculation of the ESA. The capacitive current density of the GA support decreased significantly with increasing conversion temperature, probably as a result of loss of functional groups of GA upon heating (see TGA curve of GA, Figure 4-7b). Pt/GA(800) had the lowest ESA due to higher average Pt particle size (2.9 nm). In fact, the ESA decreased more than 50% with an increase in particle size from 1.7 nm to

2.9 nm. Moreover, the ESAs of Pt/GA(400) and Pt/GA(800) were similar to the ESA values of Pt nanoparticles on other carbonaceous supports at similar average Pt particle sizes. [251] Pt/GA(600), on the other hand, had a higher ESA than that of the Pt on most of the carbonaceous supports and also than that of commercially available Pt/C. [259–263] Thus, this temperature could be associated with an optimum between the Pt particle size and GA surface chemistry effects.

The mass activities of Pt/GA samples increased with increasing Pt particle size from 27.2 mA $\text{mg}_{\text{Pt}}^{-1}$ (1.2 nm) to 30.6 mA $\text{mg}_{\text{Pt}}^{-1}$ (1.7 nm) and then decreased approximately 3-fold to 12.0 mA $\text{mg}_{\text{Pt}}^{-1}$ (2.9 nm). This trend is in good agreement with the literature where the maximum mass activities were obtained for Pt nanoparticles in the range of 1.9–2.2 nm. [251,264] Pt/GA(400) and Pt/GA(600) exhibited much higher (ca. 4–5 fold) mass activities (27.2 and 30.6 mA $\text{mg}_{\text{Pt}}^{-1}$) than the ones reported in the literature for porous graphene-derived supports showing that higher catalytic activities can be achieved via SCD, whereas Pt/GA(800) had a comparable mass activity. [265,266] SCD preserves the highly porous GA structure, which will promote growth of highly dispersed nanoparticles, whereas wet chemistry routes may damage the pore structure due to capillary pressure, especially if the solvent is evaporated under ambient conditions. Moreover, the drying step of the wet impregnation techniques often induces agglomeration of Pt nanoparticles, whereas SCD provides a more uniform distribution of Pt nanoparticles on the support with very narrow particle size distributions. [240,242,251,258] The specific activities of Pt/GA samples decreased from 6.6 $\mu\text{A cm}^{-2}$ (1.2 nm) to 2.3 $\mu\text{A cm}^{-2}$ (1.7 nm) and then significantly increased (approximately 17 fold) to 34.4 $\mu\text{A cm}^{-2}$ (2.9 nm). The specific activity values of Pt/GA(800) which was 34.4 $\mu\text{A cm}^{-2}$ was 3-times more than the specific activity of Pt/GA reported in the literature [265], whereas Pt/GA(400) and Pt/GA(600) showed smaller specific activities due to their high ESA values. Although Pt/GA(600) had the highest ESA and mass activity values among three Pt/GA samples, it had the lowest specific activity as 2.3 $\mu\text{g cm}^{-2}$. Considering the Raman results of Pt deposited samples, both $I_{\text{D}}/I_{\text{G}}$ and $I_{\text{D}'} / I_{\text{G}}$ ratios indicated an increase in the total amount of

defects in the structure with increasing conversion temperature. This may explain the highest specific activity observed in Pt/GA(800); defects present in graphene enhance the catalytic activity of Pt by lowering the O₂ dissociation activation energy and the energy barrier of the rate-determining step in ORR. [267] Additionally, the conductivity of GA increases due to thermal deoxygenation, which enhances the electron transfer between the support and the Pt particles. This could very well be the reason for the growth of particles with higher sizes, which intrinsically exhibit a higher concentration of terrace sites with higher ORR activity giving rise to higher specific activity. Furthermore, no ESA, mass and specific activity decrease was observed with continuous cycling which can be attributed to the high stability of Pt/GA electrocatalysts prepared via SCD.

6.4. Conclusions

Graphene aerogels were successfully decorated with platinum nanoparticles via the SCD technique. The average Pt particle sizes were between 1.2 and 2.9 nm, and these increased with increasing conversion temperature from 400 to 800 °C. Along with simultaneous growth of Pt nanoparticles from decomposition of the precursor, thermal deoxygenation of graphene oxide took place with a corresponding increase in the amount of defects in the structure. An enhanced ESA of 102 m² g⁻¹ was obtained for the Pt/GA(600). The ORR mass activities of the composites increased in the following order: Pt/GA(600), Pt/GA(400), and Pt/GA(800), while Pt/GA(600) and Pt/GA(400) outperformed the ORR activity of previously reported electrocatalysts prepared by a solvothermal synthesis route.[265] Lower ESA and mass activity values were observed for the Pt/GA(800) sample due to agglomeration of some of the Pt nanoparticles, which resulted in the enhanced specific activity. Overall, the average size of the Pt nanoparticles can be modified in a highly controlled fashion by the SCD technique. These composites are promising as electrocatalysts for the ORR.

Chapter 7: Conclusions & Outlook

This dissertation is devoted to the synthesis of graphene (oxide) and metal/metal oxides for applications in electrochemical energy storage devices.

The main component of the composites, graphene oxide (GO) used in this study was synthesized via modified Hummers method. The physicochemical characteristics of produced GO was analyzed by means of XRD, IR, Raman, AFM, and XPS. The results revealed that high-quality single GO nanosheets were successfully obtained with abundant oxygen functional groups. The functional groups consist of hydroxyl, epoxy, carbonyl, and carboxylic acid groups. These functional groups served as anchoring/binding sites for metal/metal oxides.

As shown in Chapter 2, electrochemical characteristics of GO was analyzed in detail with addition of first-row transition metal cations. The composite electrodes were produced by simple drop-casting method by utilization of electrostatic interactions. Results of mass-spectroscopic measurements showed that the binding between GO and metal followed the order: Fe>Co>Mn>Ni. Spectroscopic analysis revealed that the binding site for the metals were mainly C-O on GO nanosheets, rather than C=O. Electrochemical reduction increased the electrical conductivity of composite electrodes and resulted in increase in areal capacitance values (16-fold for Co/GO and Mn/GO, almost ineffective for Ni/GO and Fe/GO). Interestingly, highest areal capacitance was obtained with as-deposited Fe/GO composite (38.7 mF cm^{-2}) since electrochemical reduction was observed during the CV measurement of this sample. The analysis on variation of currents with scan rate revealed that rCo/GO and rNi/GO electrodes showed battery-like behavior whereas rMn/GO and rFe/GO exhibited pseudocapacitive properties. Consequently, cyclic stabilities of rCo/GO and rNi/GO were significantly lower than that of rMn/GO and rFe/GO.

To produce thin film composites of Ni(OH)₂/GO and SPION/GO, facile LBL assembly was utilized. Ni(OH)₂ nanosheets used in that section was synthesized via simple alkali precipitation of

Ni^{2+} salt followed by exfoliation in water. The electrical conductivity of the thin films could be enhanced by hydrazine vapor reduction while the structure of $\text{Ni}(\text{OH})_2$ in the multilayered film remained unaffected. By the power of hydrazine vapor reduction, the areal capacitance of produced multilayered electrodes increased. In fact, $r[\text{Ni}(\text{OH})_2/\text{GO}]_9$ had areal capacitance of 8.6 mF cm^{-2} at 2 mV s^{-1} . On the other hand, the growth of SPION/GO layers were monitored with UV-Vis spectroscopy and QCM. The linear increase in absorption and deposited mass confirmed the strong interaction between individual SPION and GO nanosheets. With state-of-the-art EPR measurements, it was shown that hydrazine-reduction healed all the defects in GO and nicely isolated Fe^{3+} centers were remained in a highly symmetric environment. Consequently, $r[\text{SPION/GO}]_1$ film showed extraordinary specific capacitance of 1570 F g^{-1} , which is 10-fold higher than LBL assembled iron oxide with CNT/graphene thin films reported in the literature. Overall, the hydrazine-reduction technique also caused a deterioration in the electrochemical properties of LBL-assembled thin films as supercapacitor electrodes. While as-deposited electrodes exhibited nearly perfect pseudocapacitive properties, reduced films' charge storage was limited by diffusion-related processes.

As introduced in Chapter 4, graphene aerogels were synthesized via hydrothermal treatment of GO solutions without any additive. Obtained hydrogels were dried with scCO_2 to preserve their branched mesopores which would be prone to collapse if ambient drying was utilized. As a result, GAs with high specific surface areas ($700 \text{ m}^2 \text{ g}^{-1}$) were successfully produced with an average pore diameter of 5.8 nm. This enhanced surface area is much larger than those dried with freeze-drying technique reported in the literature. It was also shown that during self-assembly of these aerogels, simultaneous deoxygenation took place. Furthermore, GAs were thermally stable under inert atmosphere, while the remained oxygen functional groups were eliminated during heating. Conversely, they decomposed completely while heating under air, around 600°C . GAs were later utilized as supercapacitor electrodes and achieved 390 F g^{-1} at 5 mV s^{-1} , approaching theoretical specific capacitance of graphene (550 F g^{-1}). Moreover, the electrocatalytic activity of metal-free

form of GA was also analyzed. In acidic electrolyte, GA gave negligible ORR activity, whereas in alkaline electrolyte, activity was observed with a $E_{1/2}$ value of 0.61 vs RHE.

In Chapter 5 and 6, synthesis of GAs decorated with metal nanoparticles were presented. Ni/GAs were synthesized via one-pot hydrothermal reaction of GO, Ni^{2+} source, and an additive to possibly bind more nickel on GA. For that purpose, various acetamides and aminoacids were added into the reaction system, where urea was chosen to be most effective in production of dispersed Ni nanoparticles and stable Ni/GA monoliths. Urea added Ni/GA was investigated systematically in terms of Ni loading. Valence band spectroscopy revealed that increase in Ni content enhanced metallicity of the composite, suppressing the conductivity of GA. Increased metallic character directly influenced the electrocatalytic properties of Ni/GA towards OER. Thus, Ni/GAs with lower Ni content exhibited inadequate activity. Ni/GA_{0.4}, on the other hand, had superior activity towards OER with a low overpotential of 320 mV to deliver 10 mA cm⁻² and high TOF of 0.11 s⁻¹. In fact, this overpotential was much lower than that of Ni/GA reported in the literature and commercial catalysts like Ru/C or Ir/C. As possible ORR electrocatalysts, Pt precursor was deposited on GA by scCO₂ assisted deposition. The precursors were converted into Pt nanoparticles by means of thermal treatment at different temperatures. The change in thermal conversion temperature tuned the particle size from 1.2 to 2.9 nm. Simultaneous deoxygenation of GA structure was reported along with growth of Pt nanoparticles. The high surface area of bare GA was preserved around 400-500 m² g⁻¹ in the presence of 30 wt% Pt with the aid of scCO₂ deposition technique. Pt/GA(600) showed enhanced ESA value, outperforming most of the Pt supported by carbon derivatives and commercial Pt/C.

Overall, this thesis work presented versatile and low-cost methods to produce two or three graphene-metal/metal oxide composites in a highly controlled fashion. The nature of metal and the effect of reduction methods on the electrochemical properties was investigated in detail supported by spectroscopic techniques. Control of particle size, dispersion, and metal content was found to be determinant in the final electrocatalytic activities of GA supported nanoparticles.

Besides, the degree of reduction (C/O ratio) of GA was another important factor for the optimal catalytic activity.



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LIST OF PUBLICATIONS

- [1] F.E. Sarac Oztuna, U. Unal, Layer-by-Layer Assembled Nickel Hydroxide and Graphene Oxide Thin Films as Electrodes for Electrochemical Capacitors, manuscript under preparation.
- [2] F.E. Sarac Oztuna, T. Beyazay, U. Unal, Facile Synthesis of Graphene Aerogel Supported Nickel Nanoparticles: Efficient and Stable Electrocatalysts for Oxygen Evolution Reaction, manuscript under preparation.
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