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ELECTROCHEMICAL STUDY OF REDUCED MULTILAYER GRAPHENE OXIDE IN AQUEOUS SUPERCAPACITORS

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ABSTRACT

Multilayer graphene oxide (GO) is a versatile two-dimensional nanomaterial that holds great promise for energy storage due to its large surface area, high chemical reactivity, and abundance of oxygen-containing functional groups. Electrochemical reduction offers an environmentally friendly and effective way to improve conductivity of GO and tailor its surface chemistry. However, the impact of different aqueous electrolytes on the efficiency of GO reduction and the properties of the resulting material is not yet fully understood. In this study, we investigate the electrochemical reduction behavior of multilayer GO in various electrolytes, including aqueous sodium nitrate (NaNO₃), lithium bis (trifluoromethanesulfonyl)imide (LiTFSI) in a water-in-salt configuration, and alkaline potassium hydroxide (KOH), focusing on their application as supercapacitor electrodes. Multilayer GO was prepared using the Hummers method and then electrochemically reduced. The electrochemical performance of the resulting electrodes was assessed through cyclic voltammetry, galvanostatic charge-discharge, and impedance spectroscopy. Morphological and elemental characterization of GO and reduced GO (rGO) were determined by employed Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS). The electrochemically reduced GO (Er-GO) electrodes demonstrated superior capacitive performance, achieving a specific capacitance of about 12 F g⁻¹ at 1.5 V under slow scan conditions, significantly outperforming the unreduced GO. These results highlight the important role electrolyte choice plays in controlling the reduction process, defect formation, and conductivity of GO. This research offers valuable insights into optimizing reduced graphene oxide materials for high-performance aqueous supercapacitors, contributing to the advancement of sustainable energy storage technologies.

Key words: Graphene oxide; Electrochemical reduced graphene oxide; Electrochemical performance; Electrodes; Specific capacitance.

1 INTRODUCTION

Graphene oxide (GO) is a highly oxidized form of graphite that contains a rich array of oxygen-containing functional groups. These groups make GO easily dispersible in water and open the door to various chemical modifications. However, GO itself is an electrical insulator, which limits its use in electrochemical applications unless it undergoes reduction to regain conductivity. However, electrochemical reduction of GO, especially under potentiodynamic conditions, has become a popular, controllable, and environmentally friendly way to convert GO into reduced graphene oxide (rGO) with adjustable properties. This reduction process gradually removes oxygen groups like hydroxyl, epoxy, and carboxyl, while restoring the graphene's π -conjugated structure. As a result, rGO shows greatly improved electrical conductivity and enhanced capacitive performance [1,2]. Recent studies have demonstrated that cyclic voltammetry (CV)-based reduction provides insight into the redox behavior of multilayer GO (MGO) and enables the correlation between reduction peaks and specific functional group removal [3-5]. Furthermore, the morphology, defect density, and electrochemical activity of rGO films are critically influenced by the number of potential cycles and the scan rate used during potentiodynamic treatment [6,7]. Understanding the detailed mechanism and kinetics of MGO reduction is essential for optimizing electrode performance in energy storage systems such as supercapacitors and batteries [8]. Therefore, this research aims to explore the electrochemical

reduction behavior of dispersed MGO using potentiodynamic techniques and evaluate the resulting structural and electrochemical modifications.

Electrochemical methods have gained considerable attention for the reduction of graphene oxide (GO), offering tunable, clean, and efficient approaches compared to conventional thermal or chemical methods. Among them, potentiodynamic techniques such as cyclic voltammetry (CV) and galvanostatic methods based on constant current application provide precise control over the reduction process, allowing researchers to systematically investigate the kinetics, electron transfer mechanisms, and capacitive behavior of multilayer graphene oxide (MGO) [9-11]. Potentiodynamic reduction enables the identification of reduction peaks associated with oxygen-containing functional groups such as epoxy, hydroxyl, and carboxyl moieties, offering insights into their removal sequence and energy barriers [12]. Furthermore, galvanostatic reduction permits continuous electron supply, minimizing potential-induced side reactions and facilitating the formation of uniformly reduced GO films with enhanced conductivity and capacitive response [13]. These electrochemical techniques not only facilitate the controlled restoration of the sp^2 carbon network but also allow in situ monitoring of redox behavior, providing a valuable platform for tailoring electrode materials for energy storage applications such as supercapacitors [14,15]. Understanding the fundamental electrochemical reduction mechanisms of MGO is thus crucial for optimizing its performance in functional energy storage devices.

Conventional reduction methods for graphene oxide (GO) primarily include chemical, thermal, and microwave-assisted techniques, each with distinct merits and limitations. Chemical reduction, particularly using hydrazine hydrate, remains one of the most widely used methods due to its high efficiency in removing oxygen-containing groups, often achieving C/O ratios above 15:1 [16,17]. However, concerns persist about the toxicity and residual nitrogen contamination of chemically reduced GO. Thermal reduction, typically performed at 300-700 °C, is advantageous for producing high-purity reduced GO (rGO) but often leads to increased defect density and requires significant energy input [18]. In contrast, microwave-assisted reduction has gained attention as a rapid and energy-efficient alternative, enabling effective GO reduction within minutes and often producing rGO with fewer defects compared to conventional thermal methods [19,20]. To mitigate environmental concerns, green reductants such as ascorbic acid and plant-derived agents have also been explored. While these alternatives offer non-toxic, sustainable options, they may require longer reaction times to reach reduction levels comparable to hydrazine [21].

In recent years, the advancement of modern reduction techniques for graphene oxide (GO) has opened new ways for the efficient and environmentally benign synthesis of rGO with tailored properties. Among these, electrochemical reduction has emerged as a particularly attractive method due to its simplicity, scalability, room-temperature operation, and the absence of harmful reducing agents [22]. It allows for precise control over reduction parameters such as potential, current density, and electrolyte composition, leading to tunable oxygen content and improved electrical conductivity of rGO [23]. Moreover, photothermal and photochemical reductions using ultraviolet (UV), infrared (IR), or visible light in the presence of photosensitizers offer a green alternative with minimal chemical waste, facilitating localized and patterned reduction suitable for flexible electronics [24,25]. Similarly, plasma-assisted reduction techniques have demonstrated rapid and solvent-free GO deoxygenation under low-temperature conditions, with enhanced surface functionality and fewer structural defects [26]. Microbial and enzymatic reductions have also attracted attention as highly selective, biocompatible processes, though scalability remains a limitation [27]. These modern methods provide not only environmentally friendly alternatives to conventional routes but also enable fine control over the structural, electrical, and chemical properties of rGO, making them highly promising for advanced applications in supercapacitors, catalysis, and biomedicine [28].

Electrochemical reduction has emerged as a promising strategy for the fabrication of rGO-based nanocomposite electrodes, particularly in supercapacitor applications, due to its environmental compatibility, scalability, and precise control over the reduction process. Compared to conventional chemical reduction methods, which often rely on toxic reagents like hydrazine, electrochemical techniques offer a green and tunable pathway for restoring the conjugated π -network of graphene

oxide (GO), while preserving or enhancing its functional surface chemistry [29,30]. When applied directly onto conductive substrates, electrochemical reduction enables the in-situ formation of conductive rGO films or nanocomposites, thereby eliminating the need for binder additives and post-processing steps [31]. This approach is particularly advantageous for constructing high-performance electrodes for supercapacitors, where the synergy between rGO and secondary materials, such as metal oxides (MnO_2 and NiCo_2O_4), conducting polymers (polyaniline), or heteroatom dopants (nitrogen), can yield enhanced capacitance, rate capability, and cycling stability [32,33]. Electrochemical reduction methods such as cyclic voltammetry (potentiodynamic) and constant current (galvanostatic) techniques also facilitate precise tuning of reduction degree and morphology, leading to optimized porosity and electron/ion transport pathways crucial for fast charge-discharge cycles [34]. Moreover, the flexibility to operate in diverse electrolytes, including alkaline (KOH), acidic ($\text{C}_6\text{H}_8\text{O}_6$ and H_2SO_4), and "water-in-salt" electrolytes (LiTFSI), further broadens the application potential of these rGO-based nanocomposites in next-generation energy storage systems [31].

Electrochemical reduction has become a favorable method for transforming graphene oxide (GO) into rGO under environmentally friendly conditions, eliminating the need for hazardous chemical reducing agents like hydrazine or sodium borohydride [35,36]. Among electrochemical methods, potentiodynamic and galvanostatic techniques are extensively used due to their ability to provide fine control over the reduction process and tune the electrochemical and structural properties of rGO [37]. Potentiodynamic reduction, typically conducted via cyclic voltammetry, offers a dynamic profile of redox reactions and allows real-time assessment of reaction kinetics, electron transfer mechanisms, and capacitive behavior [38]. It is particularly useful for fundamental studies where understanding the voltammetric response of GO and the evolution of functional groups is critical [39]. In contrast, galvanostatic reduction applies a constant current, providing a more uniform and scalable method suitable for fabricating large-area and thick-film rGO electrodes [40].

2 MATERIALS AND METHODS

2.1 Materials

The chemical reagents potassium hydroxide (KOH), potassium chloride (KCl) and sodium nitrate (NaNO_3), carbon black (C_{65} , Timcal C-ENERGY Imerys), polytetrafluoroethylene (PTFE, 60% dispersion in water) as well as ascorbic ($\text{C}_6\text{H}_8\text{O}_6$) and sulfuric (H_2SO_4 , 98%) acids with 99 % purity were obtained from Sigma-Aldrich Chemical Co. (USA). GO film was purchased from Nazarbayev University, Astana, Kazakhstan. PTF ink was purchased from Henkel Electronic Materials, Belgium, NV. Reference electrode (Ag/AgCl) and electrochemical cell holder were purchased from the USA. Ethanol and stainless steel (SS) foil were purchased from TOO "Laborfarma", Almaty, Kazakhstan.

2.1.1 Aqueous electrolytes

Molarity (M) is the most commonly used unit for expressing the concentration of a solution. It represents the number of moles of solute per liter of solution. To calculate molarity as shown in equation (1), the amount of solute (in moles) is divided by the volume of the solution (in liters) [39]:

$$M = \frac{n}{V} \quad (1)$$

Where: M ($\text{mol} \cdot \text{L}^{-1}$) is the molarity; n (mol) is moles of solute; V (L) is the volumes of solution.

The molarities of synthetic electrolytes with different chemical reagents are listed in Table1.

Table 1. Chemical composition of the different aqueous electrolytes

Chemicals	Weight, g	Molar mass, $\text{g} \cdot \text{mol}^{-1}$	Dis. Water volume, L	Molarity, $\text{mol} \cdot \text{L}^{-1}$
KOH	8.4	56	1.5	0.1
KCL	22.35	74.5	0.1	3
NaNO_3	27	108	0.25	1

2.2 Preparation of GO dispersion

Graphene oxide (GO) was used in further electrochemical studies without purification. 0.5 wt.% GO solution, measuring 50 mg of dry GO film, was prepared by mixing 10 g of deionized water with 10 g deionized water in a 20 ml glass beaker without a certain amount of PTFE binding agent. Then, the mixture was ultrasonicated for 2 h to give a stable brown dispersion. After that, the GO film was prepared by casting onto three SS foils (4x9 cm) and drying at 60 °C in the oven for 2 hours.

2.2.1 Electrochemical reduction of graphene oxide in aqueous KOH

The electrochemical reduction of the graphene oxide (GO) film was carried out by cyclic voltammetry (CV) methods in a 0.1 mol·L⁻¹ KOH using aqueous electrolyte a Potentiostat-Galvanostat (P-40X, D.C. Telemark) electrochemical workstation. A standard three-electrode configuration was constructed in the aqueous electrolyte, by using a GO-coated stainless steel (SS) foil as the working electrode, an Ag/AgCl reference electrode, and an SS foil counter electrode. The electrodes were settled in a 100 mL glass beaker containing the KOH solution, and the working electrode was polarized from 0.0 V to -1.0 V at a scan rate of 5 mV·s⁻¹ for five consecutive cycles [30,31].

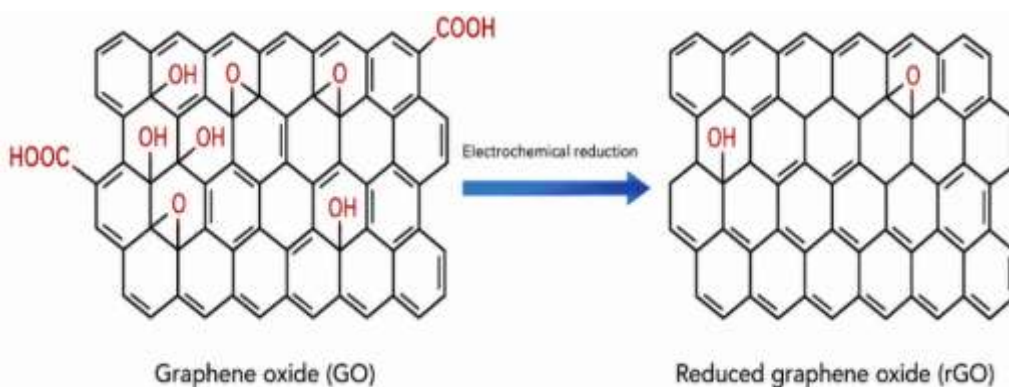


Figure 1 – Electrochemical reduction of graphene oxide (GO) in aqueous KOH

2.2.2 Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements

Investigation of capacitance in supercapacitor cell using aqueous Na₂NO₃ electrolyte electrochemical study of an electric double layer (EDL) supercapacitor cell constructed with different types of electrodes, activated carbon (AC) and rGO was evaluated using the CV and GCD measurements were performed by a Potentiostat/galvanostat (P-40X, D. C. Telemark). The CV measurements were conducted within a voltage range of 0.6-1.5 V at various scan rates. GCD testing, performed at a constant current of 0.2 A g⁻¹ with a potential limit of up to 2 mV, was used to determine the specific capacitance and energy density across different current densities. The CV curves were recorded within a 1 V potential window, while GCD tests were performed at a constant current of 0.2 A g⁻¹. Impedance measurements were conducted in the 100 kHz-10 mHz frequency range with a potential amplitude of 1.5 V. The specific capacitances were calculated from GCD curves using the following equations (2) and (3):

$$C = \frac{4I\Delta t}{m\Delta V} \quad (2)$$

Where C (F g⁻¹) is the specific capacitance; I (A) is the discharge current; Δt (s) is the discharge time; ΔV (V) is the potential window; m (mg) is the total mass of two electrodes. Specific capacitance from the CV curve was calculated using the following equation:

$$C = \frac{2}{mv(V_b - V_a)} \int_{V_a}^{V_b} IdV \quad (3)$$

Here, C ($F \cdot g^{-1}$) represents the specific capacitance, m (mg) denotes the total mass of both electrodes, v ($mV \cdot s^{-1}$) is the scan rate, I (A) refer to the discharge current, and V_b and V_a correspond to the upper and lower voltage limits in the cyclic voltammetry (CV) test [32].

2.2.3 Morphological study and elemental analysis of GO and Er-GO electrodes by scanning electron microscopy (SEM)

The SEM-EDS analysis was carried out to study the surface morphology of the electrode after drying overnight at $100^\circ C$, powder samples coated with gold nanoparticles on carbon tape using JEOL JSM-6490 LA (JEOL Ltd, Japan, 2016).

2.2.4 Preparation of working electrodes made from activated carbon (AC) and Er-GO film

The working electrodes were prepared by mixing the following mass ratios of components: 90 wt.% AC or Er-GO, 5 wt.% carbon black (conductive Acetylene Black, used as a conductive additive for anodes and cathodes of Li-ion batteries) and 5 wt.% polytetrafluoroethylene (PTFE, 60 wt.% dispersion in water, used as a binding agent). The mixture was dispersed in ethanol to form a slurry, followed by ultrasonic treatment for 10 minutes to provide a homogeneous dispersion. The electrodes were formed by rolling the carbon mixture on steel rollers to a thickness of 100-150 μm , which provided uniform material distribution and improved mechanical stability. The rolled electrodes were dried in a desiccator at $90^\circ C$ for 12 hours to remove residual moisture and solvent. After drying, the electrodes were cut with 10 mm diameter steel punches to obtain working electrode discs. Geometry was checked using a caliper and micrometer to ensure dimensional accuracy. The two electrodes were then weighed on an analytical balance for AC and Er-GO electrodes 0.00711g and the 0.0194g respectively. with an accuracy of $\pm 0.001g$ for further electrochemical studies.

3 RESULTS AND DISCUSSION

3.1 Electrochemical reduction of graphene oxide (Er-GO)

The electrochemical reduction of the GO film coated on the stainless steel (SS) foil (1x2 cm) was performed using cyclic voltammetry (CV) in a 100 mL glass beaker filled with $0.1 \text{ mol} \cdot L^{-1}$ KOH aqueous electrolyte. A standard three-electrode setup was used, consisting of an Ag/AgCl reference electrode and a 1x2 cm area stainless steel (SS) foil as a counter electrode. The CV scans were conducted from -1.000 mV to 0.0 mV at a constant scan rate of 5 mV/s for a total of five cycles, using a Potentiostat-Galvanostat (P-40X, D.C. Telemark) electrochemical workstation. Fig.2 shows visual images illustrating the transformation from graphene oxide to modified reduced graphene oxide during the step-by-step electrochemical reduction process over five cycles.

Figure 2 illustrates the electrochemical reduction of graphene oxide (GO) to electrochemically reduced graphene oxide (Er-GO). The GO film, containing oxygen-containing functional groups such as hydroxyl ($-OH$), epoxy ($C-O-C$), and carboxyl ($-COOH$) groups, was deposited onto a conductive stainless-steel (SS) foil to form the working electrode (a). The GO-coated electrode was then subjected to cyclic voltammetry (CV) at a scan rate of 5 mV s^{-1} for five consecutive cycles (c), leading to the partial removal of oxygen-containing groups and restoration of the sp^2 conjugated carbon network. Consequently, electrochemically reduced graphene oxide (Er-GO) was obtained (b), exhibiting fewer oxygen functionalities and enhanced electrical conductivity compared with the original GO film.

Figure 3 shows the cyclic voltammetry (CV) profiles of the electrochemical reduction of graphene oxide (GO) over five consecutive cycles in 0.1 mol L^{-1} KOH solution (pH 6.5-7) at a scan rate of 5 mV s^{-1} . The observed voltammograms exhibit a progressive increase in current response with each successive cycle, indicating the gradual reduction of oxygen-containing functional groups and enhancement of electrical conductivity. In the first cycle (black curve), the GO exhibits a broad cathodic current, reflecting the irreversible reduction of various oxygen functionalities, such as hydroxyl, epoxy, and carboxyl groups. This is consistent with the well-known electrochemical behavior of GO, where reduction typically occurs at potentials more negative than - 0.5 V vs. Ag/AgCl reference electrode.

As the cycles proceed (2nd to 5th), a clear enhancement in current density is observed, especially in the negative potential region, signifying an increase in conductivity due to the progressive restoration of the π -conjugated structure of graphene. The CV curves gradually stabilize by the 4th and 5th cycles (red and blue curves, respectively), suggesting that the electrochemical reduction reaches a quasi-steady state, and most of the reducible oxygenated groups have been eliminated. The shift in current density also implies improved electron transport properties of the resulting electrochemically reduced graphene oxide (ER-GO) film. The resulting ER-GO film is expected to have enhanced conductivity and improved specific capacitance for use in supercapacitors.

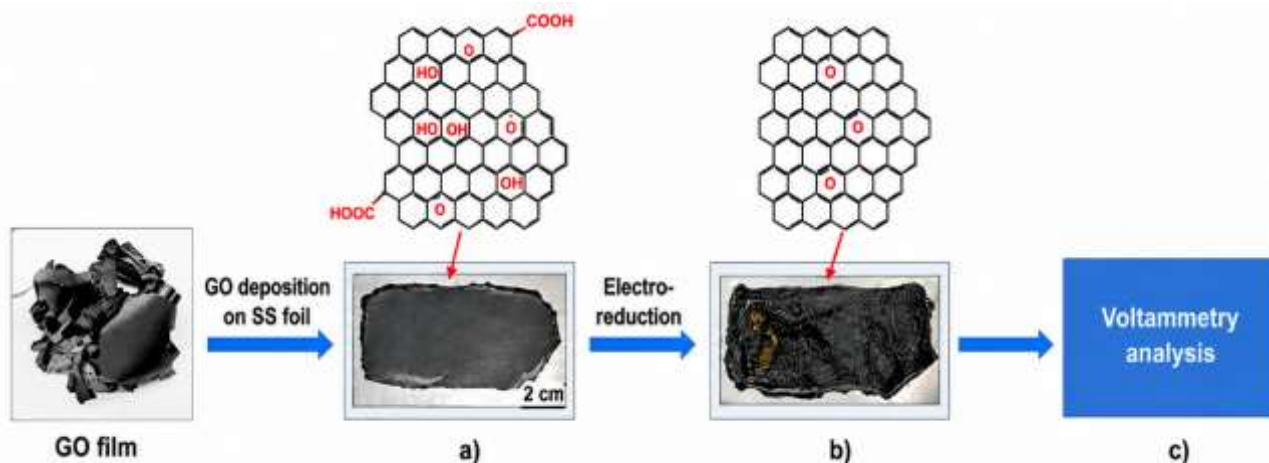


Figure 2 - Schematic illustration of the electrochemical reduction of graphene oxide (GO) to electrochemically reduced graphene oxide (Er-GO). (a) GO dispersion deposited onto a stainless-steel (SS) foil. (b) Er-GO obtained after electrochemical reduction of the GO-coated electrode. (c) The reduction was performed by cyclic voltammetry (CV) at a scan rate of 5 mV s^{-1} for five consecutive cycles

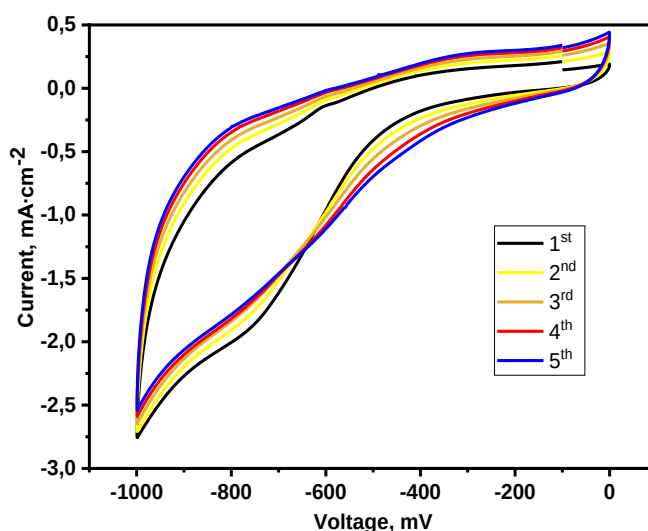


Figure 3 - CV curves of electroreduction of graphene oxide for the production of Er-GO electrode in 0.1 mol·L^{-1} KOH for (pH 6.5) from 1st to 5th cycle at a scan rate of 5 mV/s

3.2 Fabrication process for the development of activated carbon (AC) and electro-reduced graphene oxide (Er-GO) electrodes

A symmetric two-electrode configuration was employed, in which both the working and counter electrodes were fabricated from identical materials, such as activated carbon (AC) and electrochemically reduced graphene oxide (Er-GO). For comparison, two-electrode (2E Swagelok-type) supercapacitor cells were also assembled using GO and Er-GO films, with an Ag/AgCl

reference electrode and a stainless-steel foil serving as the counter electrode in selected tests. The activated carbon electrodes (AC/C₆₅/PTFE) were prepared by mixing 90 wt.% activated carbon powders with 5 wt.% carbon blacks (C₆₅) as a conductive additive and 5 wt.% polytetrafluoroethylene (PTFE, 60% aqueous dispersion) as a binder, yielding a 90:5:5 weight ratio. The mixture was homogenized using an agate mortar and pestle until the solvent had fully evaporated. The resulting composite was then dried overnight in a vacuum oven at 100 °C. Disc-shaped electrodes (10 mm diameter) were punched from the dried AC, Er-GO, and GO films, yielding final electrode thicknesses in the range of 100-125 µm. Table 2 shows the quantity of chemicals used in the test:

Table 2. Chemical compositions of used electrodes

Samples	Mass ratios of 90:5:5 wt.% electrodes			Total mass of both electrodes
	Active materials, g	C ₆₅ , g	PTFE, (60%) in H ₂ O, g	
AC	0.00711	0.000395	0.000237	0.0079
ER-GO	0.0175	0.00097	0.000582	0.0194
GO film	0.0053			0.0053

3.3 Electrochemical performance of AC electrodes with Na₂NO₃ aqueous at different voltages in a Swagelok-type cell

Figure 4 displays the cyclic voltammetry (CV) curves of a two symmetric electrode (2E) based supercapacitor cell assembled with activated carbon (AC) electrodes as working electrodes in electrodes in 1 mol L⁻¹ NaNO₃ aqueous electrolyte, recorded at a scan rate of 2 mV·s⁻¹ across various voltage windows ranging from 0.7 V to 1.5 V. At lower voltages from 0.7 V to 0.9 V, the CV curves maintain a nearly rectangular shape, characteristic of ideal electric double-layer capacitor (EDLC) behavior, where the charge storage process is dominated by non-faradaic electrostatic adsorption/desorption of ions. The symmetry and minimal distortion of the curves in these regions indicate excellent capacitive behavior and efficient ion transport within the porous structure of the AC electrodes.

As the voltage window is extended beyond 1.1 V, a gradual deviation from ideal rectangularity becomes evident, particularly at 1.3 V and 1.5 V. At 1.3 V, the current response increases significantly, suggesting the onset of additional charge storage mechanisms, possibly due to pseudocapacitive reactions or slight electrolyte decomposition. At 1.5 V, the CV curve displays a pronounced rise in current near the voltage limit, indicative of electrolyte breakdown and the evolution of gas (likely oxygen and/or hydrogen). This marks the upper limit of the cell's electrochemical stability window in this alkaline medium. The increasing current at higher potentials also indicates enhanced polarization and a departure from the predominantly electric-double-layer charge-storage mechanism. Such irreversible electrochemical reactions may contribute to increased internal resistance and gradual deterioration of the electrode–electrolyte interface during prolonged cycling.

Therefore, although a wider voltage window can theoretically increase the energy density, the associated parasitic reactions may negatively affect coulombic efficiency and cycling stability. The observed CV behavior highlights the importance of balancing the accessible voltage range with electrochemical stability when optimizing the device operating conditions. Overall, the results demonstrate that the AC electrodes operate stably up to 1.1–1.3 V with predominantly capacitive behavior. However, pushing the voltage beyond this threshold compromises stability and introduces faradaic processes that can deteriorate the long-term performance of the device. Thus, for reliable performance, an operational voltage window below 1.3 V is recommended.

Figure 5 presents the galvanostatic charge-discharge (GCD) profiles of a symmetric two-electrode cell employing activated carbon (AC) electrodes in 1 mol L⁻¹ NaNO₃ aqueous electrolyte, recorded at a constant current density of 0.2 A g⁻¹. The tests were performed across five cutoff voltages: 0.7, 0.9, 1.3, 1.5, and 1.7 V (traces shown from yellow to black). All GCD curves exhibit

highly linear and nearly symmetric triangular shapes, devoid of voltage plateaus, which is characteristic of ideal electric double-layer capacitor (EDLC) behavior. The near-perfect overlap between the charge and discharge segments at each potential window further confirms excellent electrochemical reversibility and a negligible contribution from faradaic processes.

As the applied voltage increases, the discharge duration extends significantly, from approximately 450 seconds at 0.7 V to 1450 seconds at 1.7 V, demonstrating a direct correlation between potential window and charge storage capability. This trend indicates a proportional increase in specific capacitance with voltage.

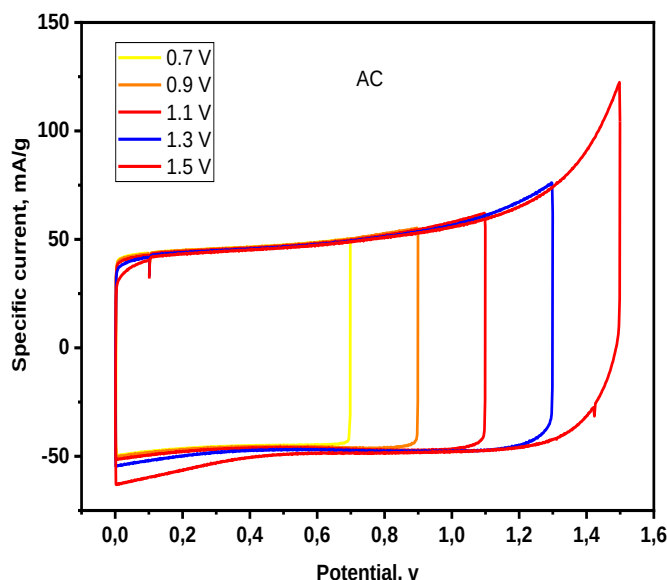


Figure 4 - CV curves of 2E cell assembled with AC electrodes in $1\text{ mol}\cdot\text{L}^{-1}$ NaNO_3 electrolyte with different voltages at a scan rate of 2 mV/s

However, a progressive increase in the initial voltage drop (IR drop) is also observed with higher voltages, rising from nearly zero at 0.7 V to approximately 0.15 V at 1.7 V. This suggests that internal resistance, comprising electrolyte resistance and electrode-electrolyte interface resistance, exerts a growing influence on performance at elevated voltages due to increased cell polarization.

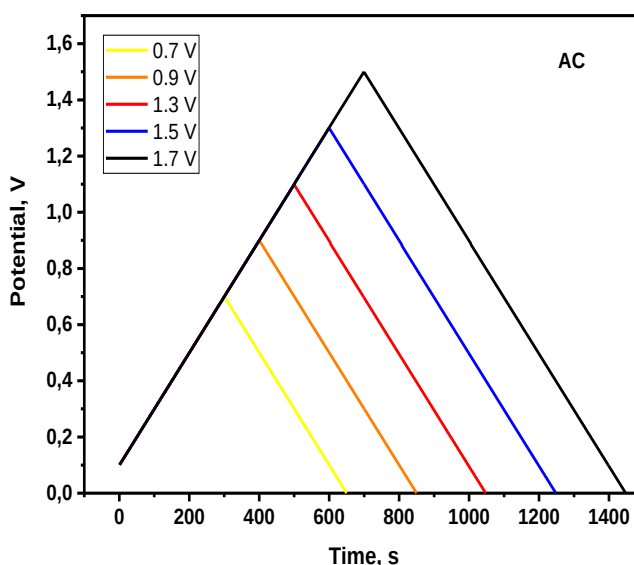


Figure 5 - GCPL curves of 2E Swagelok type cell fabricated with AC electrodes in 1 mol L^{-1} NaNO_3 electrolyte at a 0.2 A g^{-1} current density

For all cutoff voltages up to 1.5 V, the coulombic efficiency approaches 100%, indicating that the energy storage process remains predominantly capacitive with minimal parasitic reactions. However, at 1.7 V, a slight asymmetry in the GCD profile and a pronounced IR drop point to the onset of electrolyte decomposition or carbon surface polarization. These signs of electrochemical instability could impair long-term cycling stability, suggesting that operation beyond 1.5 V may not be viable for extended use. Given that energy density scales with the square of the voltage ($E = \frac{1}{2} C \cdot V$), increasing the cell voltage to 1.5 V approximately doubles the stored energy relative to 1.0 V. While extending the window to 1.7 V offers marginally higher energy, it comes at the cost of reduced reversibility and increased polarization. Therefore, operating within the range of 1.3 to 1.5 V strikes an optimal balance between maximizing energy density and maintaining long-term electrochemical stability. The AC electrodes in 1 mol L⁻¹ NaNO₃ exhibit exemplary EDLC behavior up to 1.5 V at 0.2 A g⁻¹, characterized by linear GCD profiles, high coulombic efficiency, and moderate IR drops. Although higher voltages enable greater energy storage, they introduce risks of performance degradation due to electrolyte breakdown and polarization effects. For practical supercapacitor applications, a voltage window of 1.3 and 1.5 V is recommended to ensure high energy output while preserving cycle life and stability.

3.4 Electrochemical behaviors of (Er-GO) and GO-based electrodes with Na₂NO₃ aqueous electrolyte in a 2E Swagelok type cell

Figure 6 demonstrates the cyclic voltammetry (CV) curves of a symmetric two-electrode supercapacitor cell fabricated using electroreduced graphene oxide (Er-GO) electrodes.

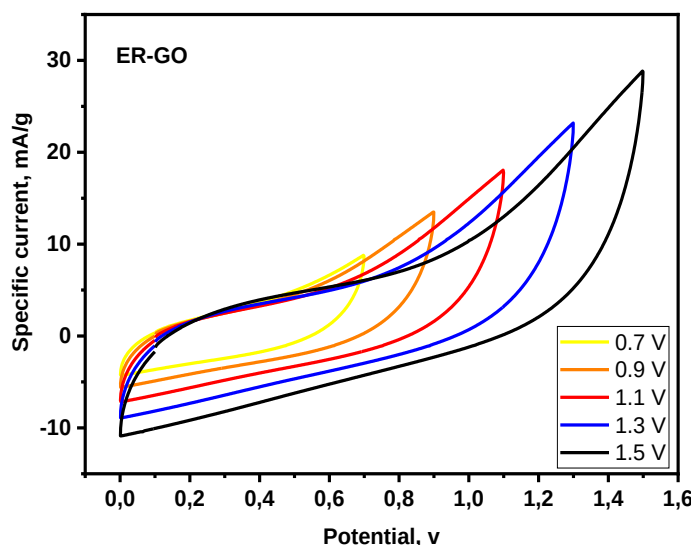


Figure 6 - CV curves of electroreduced graphene oxide (Er-GO) in a 2E Swagelok-type cell within the 1 mol L⁻¹ NaNO₃ electrolyte at a scan rate of 2 mV/s

CV measurements were performed in 1 mol L⁻¹ Na₂NO₃ aqueous electrolyte at pH 6.5, at a scan rate of 2 mV s⁻¹, over high voltage windows of 0.7 V, 0.9 V, 1.1 V, 1.3 V, and 1.5 V. The near-symmetric, quasi-rectangular shape is characteristic of an ideal electric double layer capacitance (EDLC). This suggests efficient charge distribution at the ER-GO/electrolyte interface with fast and reversible ion adsorption/desorption processes. As the voltage window increases from 1.1 V, especially at 1.3 V and 1.5 V, the CV curves broaden and become slightly distorted. These features indicate a combination of EDLC and pseudocapacitive behavior, which may be due to the residual oxygen-containing functional groups on the Er-GO surface that participate in surface redox reactions.

The specific current peaks increase in the applied voltage window, indicating a proportional increase in charge storage, with the voltage change of 0.7, 0.9, 1.1, 1.3 and 1.5 V, respectively, and the specific current densities are 10, 13, 17, 22 and 30 mA g⁻¹. This increasing trend indicates that

the Er-GO electrode is capable of storing higher energy as the operating voltage is extended, which corresponds to the quadratic relationship between energy and voltage ($E=1/2 CV^2$). The mirror-like shapes of the anodic and cathodic branches show high reversibility and minimal polarization, which are very desirable properties for energy storage systems, especially for supercapacitors. Even at the maximum voltage value of 1.5 V, the CV curve remains stable. It does not show significant hysteresis or redox peak splitting, which indicates the low intrinsic resistance and electrochemical stability of Er-GO in mild alkaline medium (KOH). CV analysis clearly shows that Er-GO is a promising electrode material for aqueous supercapacitors. Its structure provides high surface area and excellent conductivity, and partial reduction of GO introduces redox-active sites without compromising its electrochemical stability.

The ability to extend the voltage window to 1.5 V in aqueous medium is very advantageous for increasing energy density in practical applications. In conclusion, CV analysis confirms that the Er-GO electrode exhibits excellent capacitive behavior in 1 mol L⁻¹ NaNO₃ electrolyte, combining EDLC and pseudocapacitive mechanisms. Its stable operation up to 1.5 V, high specific current response, and low resistive losses clearly demonstrate that it could be a viable candidate for high-performance aqueous supercapacitors.

Figure 7 presents the galvanostatic charge-discharge (GCPL) profiles of electrochemically reduced graphene oxide (Er-GO) electrodes recorded in 1 mol L⁻¹ NaNO₃ electrolyte at a scan rate of 2 mV s⁻¹. The measurements were conducted across progressively increasing voltage windows: 0.7, 0.9, 1.1, 1.3, and 1.5 V. The potential, time curves exhibit nearly ideal triangular shapes, indicating linear but asymmetric charge-discharge behavior. The persistence of the triangular shape across all voltage ranges demonstrates high reversibility and capacitance stability of the electrode, typical for EDLC (electric double-layer capacitance) materials; however, the curves also suggest a significant contribution from pseudocapacitance. This behavior corresponds well with the nature of reduced graphene oxide, which offers a high specific surface area, good electrical conductivity, and easily accessible electrode-electrolyte interfaces for efficient charge storage. Notably, the discharge time increases with the applied voltage. As the voltage window expands to 0.7, 0.9, 1.1, 1.3, and 1.5 V, the corresponding charge durations increase progressively to 296.9, 392.8, 495.8, 594, and 694.7 seconds, respectively, while the discharge durations (Δt) similarly increase in a relatively consistent manner to 75.8, 107.3, 134.2, 167.5, and 203.1 seconds. In particular, the curve corresponding to the highest cutoff voltage of 1.5 V (black curve) displays the longest charge-discharge times, approximately 694.7 and 203.1 seconds, respectively, though these values are not symmetrical.

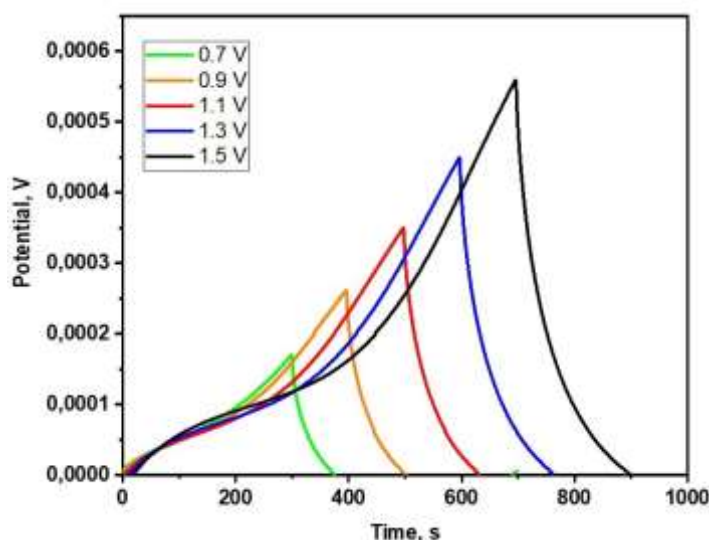


Figure 7 - Electrochemical response of electro-reduced graphene oxide (Er-GO) in a two-electrode Swagelok-type cell using GCPL in 1 M NaNO₃ electrolyte at a 2 mV/s scan rate

Figure 8 shows the Nyquist plots obtained from electrochemical impedance spectroscopy (EIS) measurements of electrochemically reduced graphene oxide (Er-GO) electrodes in a 2E Swagelok-

type cell configuration using 1 M NaNO_3 as the electrolyte. The measurements were performed at a current density of $0.2 \text{ A} \cdot \text{g}^{-1}$ and a scan rate of $2 \text{ mV} \cdot \text{s}^{-1}$ over a voltage range from 0.7 to 1.5 V. As the voltage increases, both the semicircle diameter and total impedance decrease significantly, suggesting enhanced charge transfer kinetics and improved ion mobility. At 0.7 V (green curve), the Er-GO electrode shows the highest overall impedance, with a maximum interfacial resistance of $37,460 \Omega$, indicating lower electrochemical activity and greater resistance at the electrode–electrolyte interface. In comparison, at voltages of 0.9, 1.1, and 1.3 V, the maximum impedance values decreased to $32,781 \Omega$, $11,125 \Omega$, and $8,586 \Omega$, respectively. At 1.5 V (black curve), the lowest maximum impedance was recorded at just 967Ω , indicating minimal resistance. The impedance profile at this potential still suggests some limitations in ion mobility and potential degradation of the electrode–electrolyte interface. These findings confirm the voltage-dependent electrochemical behavior of the Er-GO material and highlight its performance limitations under low-voltage conditions. To quantitatively analyze the interfacial charge transfer characteristics, the EIS data were fitted using a modified Randles equivalent circuit consisting of a series resistance (R_s), a charge transfer resistance (R_{ct}), and a constant phase element (CPE) to account for the non-ideal capacitive behavior of the double layer.

The CPE parameters (Q and n) also varied with applied voltage, indicating changes in surface heterogeneity and capacitive response. These variations suggest that elevated voltages induce structural changes at the electrode surface and the interfacial region, thereby degrading the electrochemical performance, consistent with the observed impedance trends in the Nyquist plots. Overall, the equivalent circuit analysis confirms the voltage-dependent degradation of the electrochemical properties of Er-GO.

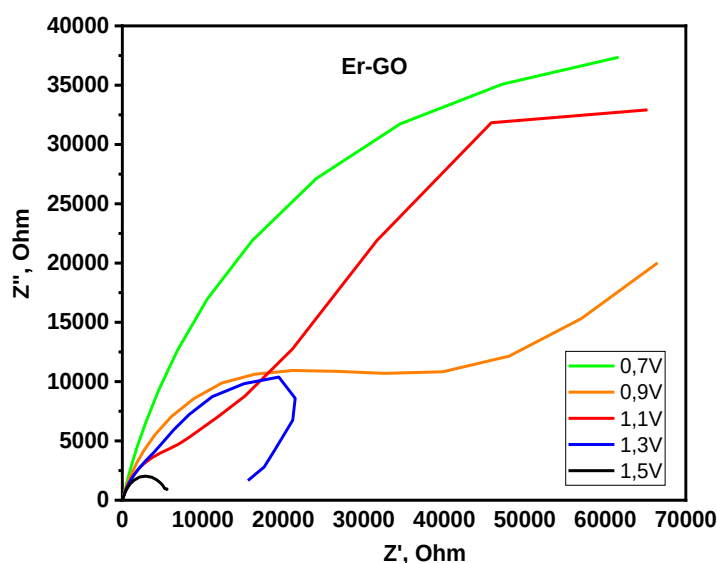


Figure 8 - Electrochemical impedance spectroscopy (EIS) of electro-reduced graphene oxide (Er-GO) in a 2E Swagelok-type cell with 1 M NaNO_3 electrolyte at a $0.2 \text{ A} \cdot \text{g}^{-1}$ current density and 2 mV/s scan rate

Figure 9 exhibits the cyclic voltammograms (CVs) of pristine (unreduced) graphene oxide (GO) electrodes recorded in 1 mol L^{-1} NaNO_3 electrolyte. These curves demonstrate a transition from electric double-layer capacitive behavior to Faradaic processes as the upper potential limit increases. The CV profiles exhibit a shape that shifts from “rectangular to exponential,” indicating limited capacitive response at low voltages and the onset of electrolysis-related reactions at higher potentials. At voltages up to approximately 1.1 V, the current remains very low and nearly constant across all scan curves, which largely overlap. This behavior reflects the low electronic conductivity of unreduced GO and the limited electrochemical activity of its oxygen-containing functional groups.

In this potential range, the formation of the electric double layer is weak, and there is virtually no pseudocapacitive contribution, highlighting the non-capacitive character of the GO film. As the

potential window expands between 0.7 V (green curve) and 1.5 V (black curve), no distinct redox peaks appear, indicating the absence of electroactive species or well-coupled redox centers on the GO surface. However, a sharp nonlinear increase in current is observed after 1.2 and 1.3 V, marking the onset of parasitic Faradaic processes. This rapid current rise is attributed to water oxidation at the positive electrode (oxygen evolution reaction) and hydrogen evolution at the negative electrode, indicating that the electrochemical stability window of GO in alkaline media is being exceeded. These findings demonstrate the electrochemical limitations of pristine GO as a supercapacitor electrode material in alkaline electrolytes. The low conductivity, weak capacitive response, and narrow stability window highlight the need for post-treatment of GO.

Specifically, electrochemical reduction (forming Er-GO) is essential to partially restore the sp^2 carbon lattice, improve conductivity, and suppress water decomposition reactions. This, in turn, enhances the capacitance and electrochemical stability of GO-based electrodes.

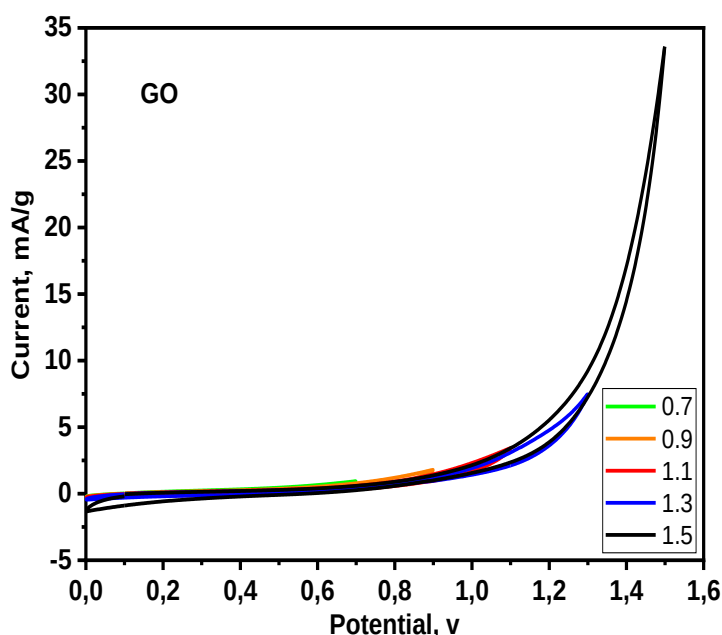


Figure 9 - Cyclic voltammetry (CV) curves recorded in a two-electrode Swagelok-type cell using GO films as both electrodes, in 1 M NaNO_3 electrolyte at a scan rate of 2 mV/s

Figure 10 exhibits the galvanostatic charge-discharge (GCPL) curves of graphene oxide (GO) electrodes measured at various cutoff voltages in a symmetric two-electrode configuration.

Across the investigated voltage range (0.7-1.5 V), the curves, especially at higher voltages, exhibit a distinctly non-linear and asymmetric shape, deviating significantly from the ideal triangular form characteristic of electric double-layer capacitors (EDLCs). This behavior reflects the low electronic conductivity and limited capacitive performance of pristine (unreduced) GO. At lower voltages (0.7 and 0.9 V), the discharge curves are short and nearly flat, with charge-discharge times of 300 and 400 seconds, and 399 and 367 seconds, respectively, indicating minimal charge storage and weak electric double-layer formation by the GO material. When the voltage window is extended to 1.1 and 1.3 V, the discharge time increases slightly to 403.1 and 464.3 seconds, respectively, but the curve shape remains non-ideal, showing a sharp voltage increase during charging and a steep drop during discharge. This response suggests the dominance of resistive behavior with limited capacitive contribution. The most pronounced feature is observed at 1.5 V, where the charge-discharge times reach 700.2 and 473.8 seconds, respectively. In this case, the voltage rapidly spikes to 0.18 mV and then sharply decreases, indicating significant polarization of the electrode and the onset of parasitic reactions, such as electrolyte decomposition or water electrolysis. This sharp voltage change confirms the electrochemical instability of GO electrodes under high voltage in NaNO_3 electrolyte. Overall, these GCPL curves reaffirm that pristine GO is unsuitable as a high-performance supercapacitor electrode material due to its low conductivity, low specific capacitance, and limited electrochemical

stability. These limitations highlight the need for subsequent electrochemical reduction of GO. Electrochemical reduction improves conductivity, restores the sp^2 carbon structure, and expands the operational voltage window, thereby enhancing the charge storage capabilities in symmetric devices.

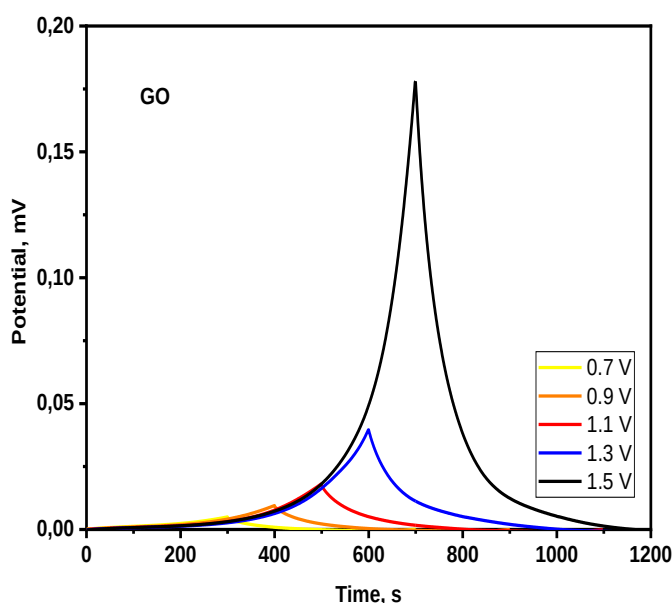


Figure 10 - GCPL curves recorded in a 2E Swagelok-type cell using GO films as both electrodes in 1 M NaNO_3 at 2 mV/s

3.5 Comparative specific capacitances of two-electrode Swagelok-type cells assembled with various graphene oxide (GO)-based electrodes in aqueous LiTFSI and NaNO_3 electrolytes

Figure 11 presents the comparative specific capacitance profiles of 2E Swagelok-type cells assembled with various graphene oxide (GO)-based electrodes: Er-GO (a) and pristine GO tested in 5 mol L^{-1} LiTFSI (b) and 1 mol L^{-1} NaNO_3 (c) aqueous electrolytes.

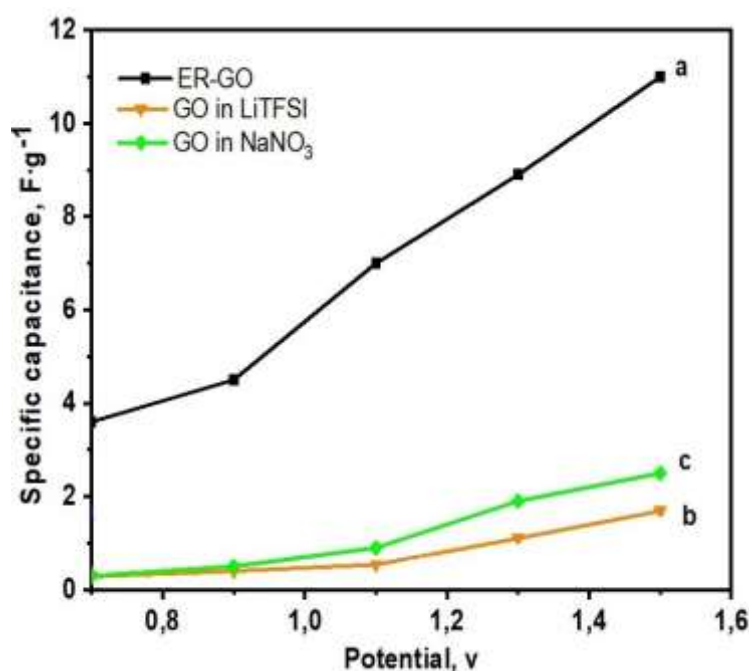


Figure 11 - Specific capacitance of 2E Swagelok-type cells assembled with electrodes of Er-GO (a), and GO in 5M LiTFSI (b) and 1M NaNO_3 (c) aqueous electrolytes, measured at a scan rate of 2 mV/s

All measurements were carried out at a scan rate of 2 mV/s. The differences in specific capacitance observed across the samples highlight the significant influence of both electrode composition and electrolyte environment on electrochemical performance. Among the electrochemical tested electrodes, the Er-GO electrode (curve a) exhibited the highest specific capacitance, increasing steadily from 3.58 F g⁻¹ at 0.7 V to 11 F g⁻¹ at 1.5 V. This enhanced performance is attributed to the efficient electrochemical reduction of GO in an aqueous KOH solution, a process that likely enables the partial restoration of the sp² carbon framework while retaining certain oxygen-containing functional groups.

Furthermore, before the reduction test, the GO electrodes tested in 5 mol L⁻¹ LiTFSI (curve b) and 1 mol L⁻¹ NaNO₃ (curve c) electrolytes exhibited intermediate performance, with specific capacitance gradually increasing as the potential increased. Interestingly, the high ionic conductivity of LiTFSI appeared to enhance the capacitive behavior despite GO was inherently low electronic conductivity. The CV curves in LiTFSI were symmetric and stable, whereas NaNO₃ showed slightly higher internal resistance, as evidenced by a more pronounced voltage lag in the GCD profiles. Therefore, the CV and GCD data, together with the specific capacitance analysis presented in Figure 17, clearly demonstrate that both the chemical reduction method and electrolyte environment play critical roles in determining the capacitive performance of GO-based electrodes. Among all tested systems, the Er-GO electrode exhibited the most promising performance in terms of specific capacitance, stability, and reversibility, making it a strong candidate for high-performance aqueous supercapacitor applications.

3.6 Morphological and elemental characterization of various graphene oxide (GO and rGO)-based electrodes by scanning electron microscopy (SEM-EDS)

3.6.1 Morphological analysis of GO and Er-GO electrodes

The surface morphology and microstructural characteristics of various graphene oxide (GO and rGO) based electrodes were examined using scanning electron microscopy (SEM), as shown in Figure 12. The pristine GO electrode (Fig. 12(a)) displays a highly ordered, layered architecture with distinct parallel alignment of the sheets, reflecting its typical lamellar structure. This morphology results from the intercalation of oxygen-containing functional groups, such as epoxides and hydroxyls, which help maintain the spacing between sheets and promote stacking without significant disruption. However, upon electrochemical reduction, as observed in the Er-GO sample (Fig. 12(b)), the electrode surface becomes noticeably rougher and more irregular. This change is accompanied by signs of partial exfoliation and structural collapse. These alterations can be attributed to the removal of oxygen functionalities, which destabilizes the sheet structure and introduces defects. As a consequence, the morphology transforms into wrinkled, crumpled, and loosely packed layers.

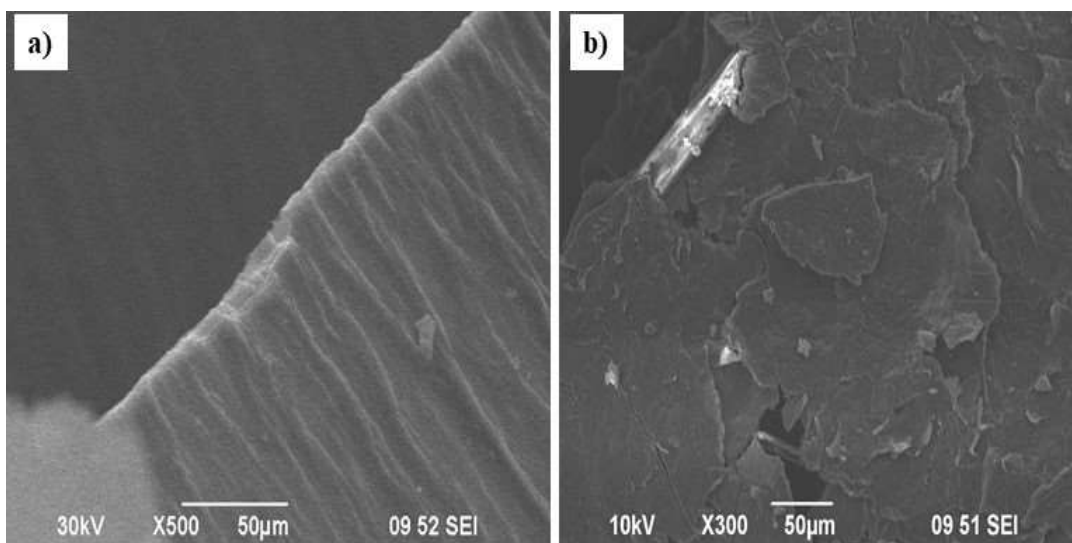


Figure 12 - SEM images of GO (a), Er-GO (b) electrodes after the electrochemical test

This new structure is beneficial because it increases the specific surface area and facilitates ion transport, thereby enhancing electrochemical performance. Although this represents a more aggressive deoxygenation process, it leads to improved electronic conductivity, even though the accessible surface area may slightly decrease. Overall, the SEM analysis confirms that the method of electrochemical reduction plays a crucial role in influencing the morphological evolution of GO, which ultimately affects the electrochemical properties of the electrodes.

When comparing chemically unreduced GO with electrochemically reduced graphene oxide (Er-GO) as shown in Figures 12 (a) and 12(b), respectively. the Er-GO sample clearly maintains a more porous and multilayer-rich architecture. This combination of porous multilayer structural integrity, large surface functionality, and accessible electroactive sites makes Er-GO (Fig. 12(b)) the most promising candidate for high-performance energy storage applications. Its morphology not only supports faster ion diffusion and higher charge storage capacity but also offers scalability and environmental friendliness in synthesis.

3.6.2 Elemental Analysis of GO and Er-GO electrodes by energy-dispersive X-ray spectroscopy (EDS)

Figure 13 presents the energy-dispersive X-ray spectroscopy (EDS) spectra of graphene oxide (GO) and electrochemically reduced graphene oxide (Er-GO), providing detailed insights into the elemental composition of the samples before and after the electrochemical reduction process. In the EDS spectrum of GO (Fig. 13(a)), prominent peaks corresponding to carbon (C K α) of 51.04 wt.% and oxygen (O K α) of 48.9 wt.% are observed. The high oxygen content confirms the successful oxidation of graphite, indicating the presence of abundant oxygen-containing functional groups such as hydroxyl, epoxy, and carboxyl groups within the graphene lattice. These groups are characteristic of GO and are responsible for its hydrophilic nature and disrupted sp² carbon framework. In contrast, the EDS spectrum of ER-GO (Fig. 13(b)) reveals a substantial decrease in the oxygen content to 35.5 wt.% and a corresponding increase in carbon content to 54.06 wt.%. This shift in elemental composition reflects the effective removal of oxygen functionalities during electrochemical reduction and the partial restoration of the sp² hybridized carbon network. Additionally, minor peaks attributed to sodium (Na K α) 1.53 wt.% and potassium (K K α /K β) of 8.86 wt.% are present, which likely originate from residual components of the KOH-based electrolyte used during the reduction process.

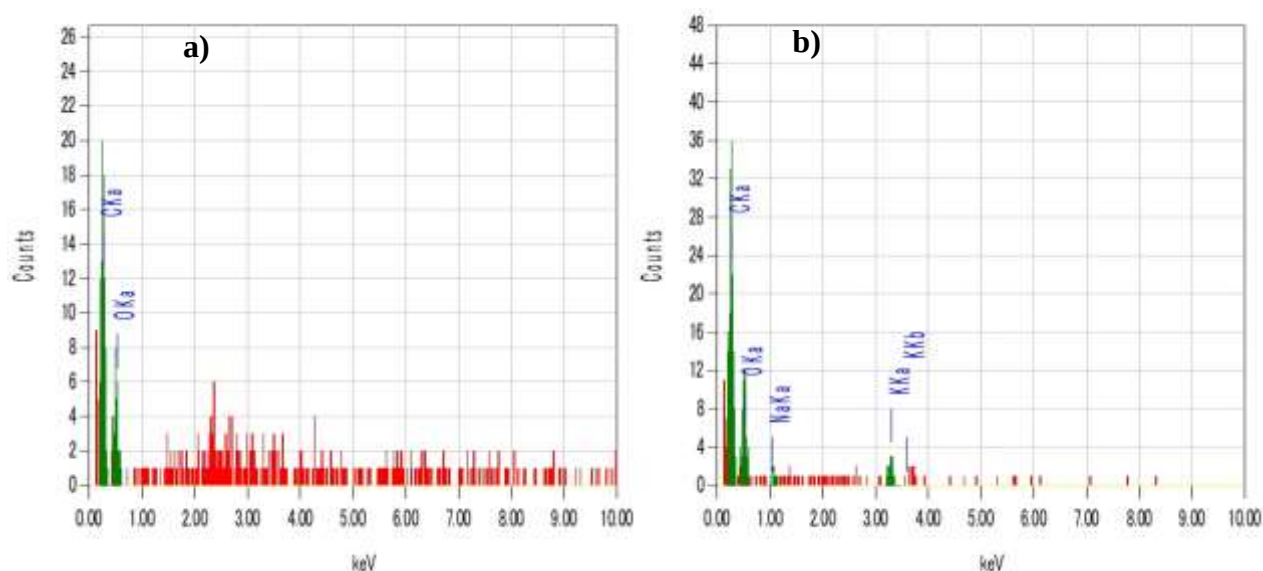


Figure 13 - Elemental composition of the GO (a) and ER-GO (b) samples determined by the SEM-EDS analysis

As shown in Figure 13 (a) and (b), the atomic percentage analysis further supports these findings exhibits the GO atomic concentrations of 58.13 at.% carbon and 41.9 at.% oxygen, consistent

with its oxidized state. Following reduction, Er-GO exhibits an increased carbon content of 64.15 at.% and a decreased oxygen content of 31.7 at.%, confirming effective deoxygenation. Trace levels of sodium of 0.95 at.% and potassium of 3.2 at.% are also detected in Er-GO, suggesting possible adsorption onto the graphene surface or intercalation between the layers during the electrochemical treatment.

Furthermore, the presence of alkali metal ions may induce doping effects or alter surface chemistry, potentially influencing the electrochemical behavior and functional performance of Er-GO. As shown in Table 3, the data confirm the successful modification of GO into Er-GO:

Table 3. Quantitative elemental analysis of GO and ER-GO samples

Elements	Analyzed materials			
	GO		ER-GO	
	Wt. %	At. %	Wt. %	At. %
C	51.04	58.13	54.06	64.15
O	48.96	41.87	35.55	31.67
K	-	-	8.86	3.23
Na	-	-	1.53	0.95
Total	100 %		100 %	

4 CONCLUSION

This study provides a thorough evaluation of the electrochemical performance of graphene oxide (GO) and electrochemically reduced graphene oxide (Er-GO) electrodes in aqueous NaNO_3 and LiTFSI “water-in-salt” electrolytes, with a focus on their potential for supercapacitor applications. The key findings can be summarized as follows:

Consequently, the results demonstrate that electrochemical reduction is an effective strategy for improving the electrochemical performance of graphene oxide (GO) electrodes. Pristine GO exhibited limited capacitive behavior because of its poor electrical conductivity and abundant oxygen-containing functional groups, whereas electrochemically reduced GO (Er-GO) showed substantially improved charge-storage characteristics, achieving a specific capacitance of approximately 12 F g^{-1} at 1.5 V. The enhanced performance of Er-GO can be attributed to the restoration of electrical conductivity, removal of insulating oxygen functionalities, and development of a porous, multilayered, defect-rich structure favorable for ion transport and charge accumulation. Furthermore, the electrolyte composition strongly affected the electrochemical response, with $5 \text{ mol} \cdot \text{L}^{-1}$ LiTFSI providing a more favorable environment for charge storage than $1 \text{ mol} \cdot \text{L}^{-1}$ NaNO_3 . These findings confirm that the combined optimization of electrode reduction, surface morphology, and electrolyte composition is essential for enhancing the performance of GO-based aqueous supercapacitors.

These findings confirm that electrochemically reduced graphene oxide (Er-GO), particularly when paired with high-performance electrolytes, holds significant promise for the development of next-generation aqueous supercapacitors with enhanced energy storage capabilities.

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Disclosure of the use of Generative AI assistance: Not applicable.

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