Li/graphene oxide primary battery system and mechanism

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Abstract
A novel type of Li/graphene oxide (Li/GO) battery based on a spontaneous redox reaction between Li metal and GO cathode is introduced as an alternative viable primary battery system. Here, we present an efficient synthesis of GO by the modified Hummers method and focus on a comprehensive study of the reduction mechanism. The Li/GO battery was thoroughly analyzed by various physical and electrochemical methods. GO rich in oxygen-bearing functional groups on graphene layers provided lithium storage sites and delivered a high discharge capacity of around 720 mAh/g at 12 mA/g. Products formed on the surface during reduction were analyzed, and a mechanism was proposed. The results uncovered the reasons underlying the improved electrochemical properties and the contribution of the irreversible capacity of reduced GO in graphene-based composite electrode materials for metal-ion batteries. The Li/GO concept is expected to shed light on the design of similar M/GO batteries based on other active metal anodes (e.g., M = Na, Mg, Al, Zn).

KEYWORDS
electrochemical reduction, Grafenika, graphene oxide, primary Li batteries, reduced graphene oxide

1 | INTRODUCTION

Primary batteries are widely known in electronic devices with low power requirements, as they are easy to construct with simple components.1 In general, ideal primary batteries must possess high specific energy and power density, good shelf-life, resistance to interference, and low cost.1 The quality and price of primary batteries depend on constituent materials: cathode, anode and electrolyte solution. Therefore, there is a need for new alternative materials with low cost and good performance to produce primary batteries in bulk quantities. Carbon-based graphene materials received high scientific interest in recent years, especially in energy and environmental applications due to their remarkable physicochemical properties.2-6 These include a high specific surface area (theoretically 2630 m²/g for single-layer graphene),2,6,7 extraordinary electronic properties and electron transport capabilities,8-10 high mechanical strength,11 and excellent thermal and electrical conductivity.12,13 According to the ISO/TS80004-13 standard of the International Organization for Standardization, graphene-based materials are monolayers of carbon atoms, consisting of one-atom-thick planar...
sheets comprising sp²-bonded carbon structures. Double-layer, three-layer, and multilayer graphene are materials consisting of two, three, and three to ten layers of carbon atoms, respectively.

Graphene oxide (GO) is a graphene derivative with rich oxygen functional groups (hydroxyl, epoxy, and carboxyl groups) attached to the basal planes and the sheet edges of graphene layers.14,15 These functional groups are attached to help in dispersion owing to high colloidal stability in the water while imparting a unique set of mechanical, colloidal, and/or optical properties.14,15 GO can be produced in desirable quantities and at a low cost. Based on its electrochemical reduction of GO, several primary and secondary battery systems were developed, for example, Li, Mg, Zn, Fe, and Cu, upon insertion of metal into GO at ambient conditions.16–20

Graphene-based materials were used in batteries as electrode materials21–27 and composite electrode materials,28,29 current collectors and their protective layer,30,31 surface coatings,32,33 and conductive additives.34 In most studies, the use of graphene-based materials demonstrates a significant improvement in the electrochemical performance of electrode materials in terms of increased discharge capacity and stabilization during cycling.21–34

There are very few reports on GO alone as a cathode material for Li batteries, where the oxygen functional groups provide lithium storage sites. The exact mechanism of lithium storage in GO is unclear. Mechanistic studies revealed that the driving force for reduction comes from releasing electrons from the metal to the GO sheets while the metal is oxidized.16–19,21,25,35–37 Concerning the mechanism of GO electrochemical reduction, there is a debate. Most researchers believe that the C–O double bonds are the lithium storage sites, whereas some argue that the epoxy groups are the main sites. In any case, the oxygen content of GO is supposed to be the key factor affecting the electrochemical performance of GO as a cathode material.25,35–37 In the present work, nanosstructured GO was used as one of the components in preparing cathode materials for primary Li batteries. This material based on graphene-like structure reveals high discharge-specific capacity due to the presence of various oxygen-containing functional groups capable of forming irreversible bonds with ions of the active material of the anode during the current-forming process (discharge). The products formed on the surface of GO during electrochemical reduction were analyzed, and a plausible mechanism is proposed herein. Besides the mechanistic studies described here, this paper opens the door for developing high specific energy, cost-effective, practical primary Li batteries.

2 | EXPERIMENTAL SECTION

2.1 | Synthesis methods

An aqueous dispersion of GO flakes (1 mg/ml) with lateral size of 0.1–4 μm and thickness of up to 1.5 nm was obtained by modified Hummer’s method as shown in Figure 1.38 In a typical synthesis, in the first stage (graphite intercalation), concentrated sulfuric acid (10 ml) was placed in a glass beaker equipped with a magnetic stirrer, followed by addition of ammonium persulfate (0.9 g) and phosphorus pentoxide (0.9 g). For complete dissolution, the resulting reaction mixture was heated to 80–85°C. To the above mixture, natural graphite powder (99.9% C, fraction 200–300 μm, 1 g) was added and stirred at a temperature of 80°C for 5 h, and then the mixture was cooled to room temperature naturally. Distilled water (250 ml) was slowly added, and the mixture was left for 7 h to allow the precipitate to settle down. The precipitate was washed several times until its pH was 7, filtered, and dried. In the second stage (oxidation of graphite), the powder obtained in the first stage (1 g) was transferred into a beaker containing concentrated sulfuric acid (40 ml), which was placed in a cooled ice bath. Potassium permanganate (5 g) was added slowly over about 2 h to the above mixture, and after 30 min, distilled water (300 ml) was slowly added while monitoring the temperature at 40°C. This stage was carried out with utmost care, over about 30 min, as temperatures above 55°C can lead to an explosion resulting from Mn₂O₇ formation. Hydrogen peroxide (30%, 10 ml) was added dropwise; during the process, bubbles were observed, and the color of the suspension changed to yellow-brown. The resulting solid precipitate was washed with deionized water several times and filtered, and the resultant powder was dried. In the final stage (dispersion of graphite oxide), the powder obtained in the second stage was added to the distilled water and subjected to ultrasonic treatment (frequency of 20.4 kHz, specific power of 0.1–1 W/cm³) for 15 min. The resulting dispersion was centrifuged for 10 min at 2000 rpm to remove large particles. Highly concentrated aqueous dispersions (hydrogels) of GO (2% mass) were obtained by centrifuging a dispersion of GO (1 mg/ml) with a Hermle ultracentrifuge at 14,000 rpm for 5 min.

2.2 | Characterization methods

The product was characterized and analyzed employing crystallographic, morphological, and spectroscopic studies. X-ray diffraction (XRD) spectra were measured using an Ultima IV X-ray diffractometer (Rigaku) with Cu Kα radiation (λ = 0.154 nm). The data were analyzed and
processed using the Jade 9 software package. Scanning electron microscope (SEM) images were acquired on a SUPRA 40 scanning electron Carl Zeiss microscope operating at 1–10 kV working voltage. Energy dispersive X-ray spectroscopy analysis was carried out on a JEOL JSM-7600F scanning microscope with an accelerating voltage of 15 kV and a resolution of up to 1 nm. IR spectra were measured with a VERTEX 70 v BRUKER FT-IR spectrometer by the attenuated total reflectance method using a PIKE GladATR attachment with a spectral resolution of 4 cm. Raman spectra were acquired using a Renishaw In Via spectrometer (Great Britain) using a 514 nm laser for excitation. The spectrometer was calibrated on a standard monocrystalline silicon sample with a fundamental vibrational mode at 520.5 cm\(^{-1}\). X-ray photoelectron spectroscopy (XPS) spectra were obtained on an Axis Ultra DLD spectrometer (Kratos) using monochromatic Al K\(\alpha\) radiation at an X-ray gun power of 150 W. Survey and high-resolution spectra were recorded at transmission energy of 160 and 40 eV and step size of 1 and 0.1 eV, respectively. To eliminate the effect of sample charging, spectra were recorded using a neutralizer. Elemental analysis (C, H, N, S(O)) was performed on an automatic analyzer Vario Micro cube. The combustion temperature of the sample was 950°C. C, H, N, S(O) content was calculated automatically by the instrument software. Thermogravimetric analysis (TGA) was carried out on a TGA/DSC thermal analyzer SDT Q600.

All electrochemical studies of primary Li/GO cells were performed using pouch cells under similar experimental conditions. GO foams were glued to aluminum (Al) foils current collectors using a primer (CB/CMC = 5/95 by weight) as shown in Figure 2. Al foils (40–60 mm) were used as substrate (current collectors), and the loading level of the GO electrode was 2.7–3.0 mg/cm\(^2\). The electrodes were dried at 70°C under ambient conditions and transferred into a high-purity argon atmosphere using a PureLab HE glovebox for the fabrication of Li/GO pouch cells. The SelectiLyte LP40 electrolyte solutions comprising ethylene carbonate, diethyl carbonate (EC/DMC 1:1 v/v) and 1 M LiPF\(_6\), and a Dreamweaver Silver ARTM40 separator were used for the fabrication of electrochemical cells and battery prototypes. To examine the changes in GO structure during the electrochemical reduction in the

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**FIGURE 1** Schematic representation of the preparation of highly concentrated aqueous dispersions of GO (hydrogels). GO- graphene oxide.
discharge process, postmortem analysis was carried out by removing the electrodes from the discharged cell for further analysis. The discharge of cells was carried out to voltages of 2.5, 2.0, 1.5, and 1.0 V versus Li/Li+ by electrochemical battery tester "Neware." Upon completion and during of the discharge process, a Biologic potentiostat/galvanostat (model VMP3) was used for electrochemical impedance spectroscopy (EIS) analysis with an amplitude of 5 mV around equilibrium in the frequency range of 0.01 Hz to 100 kHz.

3 | RESULTS AND DISCUSSION

GO is a chemically modified graphene, which may be obtained by oxidation and exfoliation of graphite by the modified Hummer’s method. As shown in Figure S1, it is a monolayer of carbon atoms having both (largely) sp2-hybridized carbon atoms and (partially) sp3-hybridized carbon atoms containing oxygen functional groups located both on the basal (hydroxyl and epoxy) and on the edge plane (carboxyl, carbonyl, phenolic, lactone, and quinone). GO is a dielectric, but it has hydrophilicity, proton conductivity, high reactivity, and the ability to change the stoichiometric composition. The formation of GO was examined by various spectroscopic and microscopic techniques such as powder XRD, SEM, XPS, and atomic force microscopy (AFM) studies, as discussed below.

The XRD pattern of the synthesized GO is shown in Figure 3A, where a broad peak of (002) reflection at 2θ = 10.3° indicates the expansion of the interlayer distance. The calculated interlayer separation is 9 Å, in good agreement with literature prepared by the modified Hummers method. The SEM of pristine GO and GO electrode samples (Figure 3B, C, respectively) display a flaky morphology. The XPS C1s deconvoluted spectra of the GO sample (Figure 3D) shows four characteristic peaks at 284.5, 285.3, 286.6, and 288.8 eV for sp2 hybridized C, sp3 hybridized C, epoxy, carboxyl, and carbonyl group moieties, respectively. They were fitted to Gaussian-Lorentzian peak shape after performing a Shirley background correction. AFM measurements were carried out to investigate the surface morphology. For AFM imaging, GO was dispersed in ethanol and the film was coated on the microscope glass. The thickness measured from the AFM image ~1.5 nm (Figure 3E), corresponds to a single layer of GO. TGA of GO is shown in Figure 3F, where the GO sample was heated in air at a rate of 10°C/min up to 800°C. The reduced GO was initially obtained during the heating process, which is oxidized to CO2 upon further heating. The GO sample showed ~10% weight loss at up to 100°C due to the removal of water molecules trapped between the GO sheets, followed by ~25% weight loss at 200°C, possibly due to pyrolysis of the functional groups, released as CO, CO2, and steam. Finally, there is a ~30% weight loss at 600°C due to the combustion of the carbon skeleton of GO (Figure 3E). The elemental analysis shows C (58.0 ± 1.0%), H (1.5 ± 0.5%), O (39.0 ± 1.0%), and trace amounts of sulfur (less than 0.05%), which probably come from the preparation procedure. These results are in agreement with reported values.
Electrical conductivity is one of the key requirements for electrode materials. To achieve the desired values, different conductive additives (carbon black, graphite) are integrated into the electrode active material. However, GO is known as a dielectric material, and in this study, it was used without any conductive additives. As described previously,39–41 depending on the humidity or type of solvent, GO can show features of ionic conductivity. Thus, when immersed in an electrolyte solution, GO can transfer charge, which is a sufficient condition to start the process of electrochemical reduction, during where the material acquires an electronic type of conductivity.19,20 To better understand the electrochemical reduction process, GO samples were subjected as cathode materials for Li primary batteries. Figure 4A displays the voltammogram of GO at scan rates of 0.5 and 1 mV/s at the potential window between open-circuit voltage (OCV ~3.5 V) and 1.0 V versus Li/Li+. A characteristic reduction peak appeared at 1.7 V versus Li/Li+ during discharge regardless of scan rate. The GO electrodes were subjected to discharge at different C rates, namely C/50, C/25, and C/10 under the same conditions. Voltage profiles are shown in Figure 4B. The OCV of the cell before discharge was around 3.4 V.
versus Li/Li\(^+\). Upon initiation of galvanostatic discharge, there was a sudden decrease in the cell voltage followed by a plateau around 2.5–2.3 V, and a gradual decrease to the cut-off voltage of 1.0 V for C/50 to C/10 rates. The Li/GO cells delivered a specific capacity of 721, 687, and 626 mAh/g for C/50, C/25, and C/10, respectively, quite close to the theoretical value (910 mAh/g), which was calculated on the basis of GO. In the current density calculations, the “C” rate was set as 600 mAh/g. As shown in Figure 4C the Li/GO cells can be subjected to high specific currents from 10 to 200 mA/g, during the discharge process, the results concluded that Li/GO cells withstand high specific currents and are expected to be useful for a range of power densities. Furthermore, Li/GO cells were evaluated for pulse power studies as shown in Figure 4D, where the cells were discharged at 20 mA/g with pulse-specific current of 120 mA/g for 1 min at regular intervals of 0.5 h of discharge. The voltage decreases at pulse current of 120 mA/g, but increases back to the normal discharge plateau once the current is decreased to 20 mA/g. Furthermore, the discharge capacity of GO depends strongly on the content of oxygen functional groups and on the surface area (Tables 1 and 2, respectively). The surface area was measured by N\(_2\) adsorption isotherms as shown in Table 1. The presence of functional groups and the content of oxygen can be controlled and thereby, the properties of the GO materials can be tuned as reflected in the data presented by Table 2.

GO foam shows more intensive electrochemical reduction than GO film or graphite oxide electrodes. As electrochemical reduction is a surface chemical reaction, the extent of reduction depends mainly on the interlayer distances. In the case of GO film or graphite oxide electrodes, the interlayer distance is 9 Å, and the size of the lithium ions in the solvation shell is around 10 Å (Figure 5A), which cannot reduce the functional groups in between the graphene layers. In GO foam, on the other hand, the layers are randomly aligned (Figure 5B). Therefore more functional groups have access to reduction with the insertion of Li ions which compensate the negative charge that the electrode receives upon reduction.

Li/GO nonaqueous primary cells were assembled, subjected to discharge at 50 mA/g current density, and
studied by EIS at initial and several discharged potentials as shown in Figure 6. The depth-of-discharge (DOD) is defined as the ratio between the charge removed from the cell by discharge and the total capacity of the cell. The variation of impedance parameters with DOD was studied to identify the cell’s state of charge. Nyquist plots of fresh and fully discharged Li/GO cells shown in Figure 6 consist of a high frequency intercept on the real axis, a semicircular region between 100 kHz to 0.01 Hz, and a linear region is parallel to the real axis. Two overlapping semicircles are observed at the initial stages, while well-separated semicircles are seen at higher DOD (discharged below 2.3 V, down to 1.0 V). From the Nyquist plots, the cell resistance decreases from 1000 to 239 Ω during the initial discharge to 2.3 V, and further decreases to 217 Ω at ensuing lower discharge potentials. The substantial decrease in $R_{ct}$ indicates that the progressing lithiation of these electrodes facilitates better accessibility of the nonaqueous electrolyte solution to active surface sites (oxygen-based functional groups). The better separation is more facile, as expected after dielectric rupture of the surface films, which frees a large fraction of the Li surface from the film, decreasing its resistance. The increase in the resolution of the spectra at higher DOD ($\leq2.3$ V versus Li/Li$^+$), namely, the appearance of two semicircles instead of one, reflects also the change in accessibility of reduction sites, the formation of surface films comprising LiF and AlF$_3$ on the GO surface, confirmed analytically and discussed in the following sections.

### TABLE 1

| Surface area (m$^2$/g) | Discharge-specific capacity (mAh/g) |
|-----------------------|-----------------------------------|
|                       | Rate (C/10) | Rate (C/25) | Rate (C/50) |
| 15.3                  | 404         | 523         | 547         |
| 20.5                  | 467         | 565         | 626         |
| 26.7                  | 513         | 626         | 643         |

Abbreviation: GO, graphene oxide.

### TABLE 2

| Oxygen content (%) | Hydrogen content (%) | Discharge-specific capacity (mAh/g) |
|-------------------|----------------------|-----------------------------------|
|                   |                      | Rate (C/10) | Rate (C/25) | Rate (C/50) |
| 26.4              | 1.7                  | 367         | 415         | 483         |
| 41.1              | 1.9                  | 452         | 492         | 519         |
| 41.8              | 2.2                  | 514         | 623         | 647         |
| 46.65             | 2.4                  | 626         | 687         | 721         |

Abbreviation: GO, graphene oxide.

### 4 MECHANISTIC STUDIES

Several characterizations are compared before and after the electrochemical process to understand the mechanism of electrochemical reduction. Figure 7 shows the surface structure before and after discharge. As evident from Figure 7B, after discharging to 2.5 V, individual nanoparticles with an average size of 20 nm are formed on the surface of GO as shown in Figure 7A. The number of observed nanoparticles increases when the discharge process proceeds up to 2.0 V (Figure 7C). A significantly dense layer of particles is observed when a voltage of 1.5 or 1 V is reached (Figure 7D,E). In the process of electrochemical reduction, the reaction products are formed.
FIGURE 6  EIS characterizations of a typical Li/GO cell at different depth-of-discharge at potentials of open-circuit voltage, 2.5–2.0, 1.7, 1.5, and 1.0 V and discharge voltage profile of the Li/GO cell with selected points. The impedance spectra are presented as Nyquist plots.

FIGURE 7  Scanning electron microscope images of graphene oxide (GO) surface (A) before and after discharge to (B) 2.5, (C) 2.0, (D) 1.5, and (E) 1 V. The energy-dispersive X-ray spectroscopy analysis of GO surface (F) before and (G) after electrochemical reduction, showing, from left to right (F1, G1) SEM photomicrographs, (F2, G2) local energy-dispersive spectra, and (F3, G3) elemental content.
on the surface of GO (Figure 7B–E). To study the composition and structure of the products, an analysis of GO samples was carried out before and after electrochemical reduction (discharge was performed to a voltage of 1 V) by SEM with an energy-dispersive X-ray spectroscopy (EDX) extension (Figure 7F1–G1–3). According to the EDX results, the initial samples of GO contain carbon, oxygen, and trace amounts of manganese and sulfur originating from potassium permanganate and sulfuric acid used in the synthesis of GO (Figure 7F1–3). After electrochemical reduction, a significant decrease in the carbon content was measured due to the formation of a continuous coating of reaction products on the GO surface (Figure 7G1–G3), such as LiF, AlF3, and so forth. In addition, significant amounts of oxygen were detected, as well as phosphorus and fluorine, from the LiPF6 salt, which was used as an electrolyte. Please note that EDX analysis does not allow the detection of elements with low atomic weight such as Li and hydrogen.

In addition to energy-dispersive analysis, samples were also studied by Fourier-transform IR spectroscopy (FTIR) (Figure 8). Spectra obtained before and after electrochemical reduction substantially differ from one another. There are no peaks characteristic of adsorbed water, carboxyl, and hydroxyl groups at 3000–3800 cm$^{-1}$. After reduction, carbonyl (1726 cm$^{-1}$) and hydroxyl (1409 cm$^{-1}$) groups were obtained. Low-intensity peaks for C=O (1652 cm$^{-1}$) and epoxy groups (1085, 1160 cm$^{-1}$) were preserved, but distinct high-intensity peaks at 467 and 500 cm$^{-1}$ characteristics of LiF were also obtained at 710 cm$^{-1}$ for LiPF6 and 978 cm$^{-1}$ for POF3.42–44

Figure 9A,B presents XRD data of samples before and after electrochemical reduction, respectively. The broadened reflection at the 11–13° 2θ range, corresponding to GO, can be identified for the initial sample. After electrochemical reduction, a peak in the 11–13° 2θ range is not observed in the samples. However, a distinct peak at 23° is formed, which is characteristic of reduced GO. Two weak peaks at 55° and 68° appear, corresponding to both Li2O and LiOH.45,46 As cathodes based on GO were fabricated on the surface of aluminum foil, the XRD spectra also contain reflections of Al phases, which correspond to 38°, 42°, 44°, 65°, 78°, 81°, 99°, 112°, and 116°. An increase of intensity at 42° and reduction in intensity with

![Figure 8](image-url)  
**Figure 8** IR spectra of graphene oxide samples before (A) and after (B) electrochemical reduction
broadening of the peak at 38° after GO recovery can probably be explained by AlF$_3$ and LiF formation on the Al current collector due to the reduction of electrolyte solution species as part of the overall discharge processes. XPS analysis of the samples (Figure 9C,D) revealed the presence of F1s, C1s, O1s, P2p, and Li1s peaks in the photoelectron spectra of reduced cathodes. According to published data, the deconvolution of the F1s spectrum (Figure 9E) demonstrates the presence of LiF and Li$_x$PF$_y$. The deconvoluted spectra of C1s (Figure 9F) clearly show GO reduction when compared to those of C1s before electrochemical reduction (Figure 3D).
Thus, according to the results of in-situ structural studies and based on published data, it is clear that the process of electrochemical reduction of GO consists of the interaction of oxygen-containing functional groups with Li$^+$ ions. Therefore, it is first necessary to analyze the bonding energy of oxygen-containing functional groups to understand the sequence of their recovery (Table 3). Kim and coworkers calculated the binding energies of epoxy and hydroxyl groups, indicating that the epoxy is much more stable than the hydroxyl group (62 vs. 15.4 kcal/mol).

Elemental analyses, IR, XRD, and XPS confirm the presence of lithium fluoride. It is well known that EC, EMC, and PF$_6^-$ anions are reduced irreversibly at potentials below 1.6 V versus Li in the presence of Li ions. ROCO$_2$Li, ROLi species, Li$_2$CO$_3$, LiF, Li$_x$PF$_y$, and Li$_x$POF$_y$ moieties are relevant reduction products. The irreversible reduction process of the solution in our cells is not massive because the cathodic polarization of the GO cathodes is limited to 1 V versus Li to fit the potential window of practical Li/GO batteries. However, part of the capacity of the cathodes should be assigned to these side reactions, which in the present case are not problematic, since anyway, we deal with primary Li batteries. The spectroscopic data reflect the above side reduction of the electrolyte solutions, showing the presence of LiF and phosphorous containing species (Figure 9). It should be noted that the presence of a functional group on the GO surface facilitates the formation of hydrogen bonds with intercalated water molecules (Figure S2). The water content can reach 8–12 wt%, as evidenced by the TGA results (Figure 3F). Hence, their presence enables further interactions with the LiPF$_6$ electrolyte as suggested in the scheme of Figure S3.

Hereby, the immersion of GO in an electrolyte solution leads to the formation of HF. Furthermore, when the electrochemical potential is shifted to the negative range (Figure 4A), lithium ions and hydroxyl functional groups interact with the formation of LiOH, which in turn reacts with HF to form LiF and H$_2$O (Figure 10A). With a further shift of the electrochemical potential to the negative range, epoxy groups react with lithium ions to form Li$_2$O, which, in turn, further reacts with HF to form LiF and H$_2$O (Figure 10B). Therefore, the process of electrochemical reduction of GO is accompanied by an increase of the water content in the electrolyte solutions. To verify this mechanism, an analysis of the electrolyte humidity in the electrochemical cells before and after discharge (electrochemical reduction) was performed (according to the Fisher’s method). The results (Table 4) confirm the alleged judgment.

Accordingly, the current-forming process during the discharge of the primary chemical element system Li/LiPF$_6$, EC:DMC|GO can be described by the reactions shown in Figure 10. According to the proposed mechanism, reducing the hydroxyl group used one electron, while reducing the epoxy group requires two electrons. The theoretical capacity of GO can be calculated. The total hydrogen content for the GO sample (Table 5) is 2.40 wt%, while the sample contains 11.41 wt% of water (Figure 4F). According to the calculations, the content of hydrogen in GO that comes from the water is 1.25%. Therefore, the hydrogen content, related to functional groups, will be 1.15%. For easy calculation, it can be assumed that 1.15% of the hydrogen coming from hydroxyl groups. According to the proposed mechanism

### TABLE 3
Average bond energy and length of covalent bonds in GO

| Bond     | C atom hybridization | Energy (kJ/mol) | Length (nm) |
|----------|----------------------|-----------------|-------------|
| C=O      | sp$^2$               | 620             | 0.133       |
| C=O      | sp$^3$               | 344             | 0.143       |
| C=O      | sp$^2$               | 708             | 0.121       |
| O-H      | —                    | 460             | 0.096       |

Abbreviation: GO, graphene oxide.

### TABLE 4
Content of H$_2$O in the electrolyte

| H$_2$O (ppm) | Initial electrolyte | After holding the GO electrode for 24 h | After discharge |
|--------------|---------------------|----------------------------------------|-----------------|
|              | 73                  | 170                                    | 735             |

Abbreviation: GO, graphene oxide.

### FIGURE 10
Electrochemical reduction of graphene oxide by reduction of (A) hydroxyl and (B) epoxy groups

### TABLE 5
Results of CHNS(O) elemental analysis of graphene oxide samples

| C–, H–, N–, S– (%) | C– | H– | N– | S– |
|--------------------|----|----|----|----|
| 46.9               | 2.4| 0.5| 3.55|

Abbreviation: GO, graphene oxide.
| Cell type   | Electrochemical reaction       | Molecular weight | Valence change | Theoretical cell voltage (V) | Theoretical capacity (Ah/kg) | Theoretical energy density (Wh/kg) | Theoretical energy density (Wh/L) |
|-------------|--------------------------------|------------------|----------------|-----------------------------|-----------------------------|-----------------------------------|-----------------------------------|
| Li/MnO₂     | MnO₂ + Li → LiMnO₂             | 86.9             | 1              | 3.5                         | 310                         | 1540                              | 1005                              | 4235                            |
| Li/SO₂      | 2SO₂ + 2Li → Li₂S₂O₄           | 64               | 1              | 3.1                         | 418                         | 600                               | 1170                              | 1650                            |
| Li/SOCl₂    | 2SOCl₂ + 4Li → S + SO₂ + 4LiCl | 119              | 2              | 3.65                        | 450                         | —                                 | 1470                              | —                               |
| Li/SO₂Cl₂   | 2SO₂Cl₂ + 6Li → Li₂SO₄ + S + 4LiCl | 135             | 2              | 3.91                        | 397                         | —                                 | 1405                              | —                               |
| Li/CuF₂     | CuF₂ + 2Li → 2LiF + Cu         | 101.6            | 2              | 3.54                        | 530                         | 1520                              | 1650                              | —                               |
| Li/I₂       | I₂ + 2Li → 2LiI               | 253              | 1              | 3.1                         | 211                         | —                                 | 591                               | —                               |
| Li/Ag₂CrO₄  | Ag₂CrO₄ + Li → Li₂CrO₄ + 2Ag   | 331.8            | 2              | 3.1                         | 160                         | 900                               | 515                               | —                               |
| Li/CuS      | CuS + 2Li → Li₂S + Cu         | 95.6             | 2              | 2.15                        | 560                         | 2570                              | 1050                              | —                               |
| Li/FeS₂     | FeS₂ + 4Li → 2Li₂S + Fe       | 119.9            | 4              | 1.8                         | 890                         | 4350                              | 1304                              | —                               |
| Li/CFₓ      | (CFₓ)ₙ + nLi → nLiF + Cₓ      | 31               | 1              | 3.1                         | 864                         | 2330                              | 2180                              | 5942                            |
| Li/GO (Grafenika) | GO + 2Li → RGO + Li₂GO + 2Li → RGO + LiOH | 2043            | 2              | 2.5                         | 910                         | ~1830                             | 2285                              | ~4575                           |
(Figure 10A), one electron is responsible for the reduction of –OH groups, so the amount of electric charge can be calculated from the amount of substance (hydrogen). Thus, restoring the –OH groups in 1 g of GO corresponds to around 300 mAh/g GO. Let us suppose that the total oxygen content according to the CHNS(O) analysis is 46.65% (Table 5). The content of oxygen corresponding to the epoxy group can be calculated as total oxygen content (46.65%) minus the oxygen coming from water (10.15%) and the hydroxyl groups (18.2%). According to the proposed mechanism (Figure 10B), two electrons participate in the reduction of epoxy groups. Respectively, according to the amount of substance (oxygen), the amount of electric charge can be calculated, corresponding to around 610 mAh/g GO. Thus, according to the proposed mechanism, a complete electrochemical reduction of 1 g of GO will require around 910 mAh.

As a final discussion, it is interesting to compare the Li/GO battery system described herein to other commercial primary Li battery systems to evaluate its practical importance. Table 6 provides such a comparison. There are several different types of primary Li battery technologies that are available, commonly used today for a variety of applications. The comparison reflected by Table 6 seems to show that the Li/GO battery system described herein has a chance to compete well and outperform with already known and used commercial primary Li battery systems. We can conclude that further optimization work that will include cost effects can lead to the successful development of new effective high energy density and revolutionize the use of greener primary Li/GO battery systems.

5 CONCLUSIONS

Based on the spontaneous redox reactions of a novel type of Li/graphene oxide (Li/GO) system, a primary battery was demonstrated along with a comprehensive study of the electrochemical reduction of the GO cathodes. The GO cathode material was prepared by the modified Hummers method and thoroughly characterized by various methods. The oxygen-containing functional groups on the graphene layers serve as lithium storage sites and deliver a high discharge capacity of about 720 mAh/g at a current density of 12 mA/g. The mechanism of the electrochemical reduction was proposed by in situ analysis where two electrons participate in the reduction of the epoxy groups, which are the main lithium storage sites. The results disseminated the reasons for the electrochemical improvement and mechanism of redox reactions in GO electrode materials of Li/GO batteries and are expected to provide a strong starting point for the development of new practical high energy density primary Li/GO batteries.

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CONFLICT OF INTERESTS

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data will be made available with a reasonable request to the corresponding author.

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SUPPORTING INFORMATION

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