

Research papers

Reduced-graphene-oxide-enhanced nanostructured lead–acid batteries: Performance optimization and life cycle assessment

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ABSTRACT

The integration of nanostructured materials into energy storage systems is a promising approach to improve lead–acid battery performance. This study examines the effect of reduced graphene oxide additives on twelve-volt lead–acid batteries, focusing on key metrics including energy density, charge–discharge efficiency, and cycle life. Batteries with and without reduced graphene oxide were tested in five-molar sulfuric acid using an absorbed glass mat separator in a zero-gap configuration. The electrodes were subjected to deep cycling with a low cut-off voltage, and charge–discharge tests were performed at a high rate corresponding to ten times the nominal capacity rate. The results show that adding reduced graphene oxide improves charge retention and stabilizes battery behavior under high-rate operation. Scanning electron microscopy revealed substantial differences in electrode morphology before and after cycling: the initial nanowire structure was no longer observed and the surface was largely covered by lead sulfate crystals, while a porous morphology was retained. Post-cycling X-ray diffraction and Raman spectroscopy confirmed that not all active material converted to lead sulfate under the applied conditions. Additionally, the environmental impact of the manufacturing process was assessed using Life Cycle Assessment methodology for laboratory-scale electrodeposited electrodes, revealing that reduced graphene oxide has a limited environmental impact while enhancing performance.

1. Introduction

Lead–acid batteries (LABs) are among the most widely deployed energy storage technologies because of their reliability, low cost, mature manufacturing, and high recyclability [1,2]. Despite their long-standing market presence, their use in applications requiring frequent high-power transients and rapid charge–discharge operation remains constrained by intrinsic limitations, including relatively low energy density (30–40 Wh kg^{−1}) [3,4] and limited cycle life under demanding conditions, typically around 500 cycles [5,6]. These constraints make their use challenging in hybrid electric vehicles and renewable energy applications [7,8].

Performance degradation is accelerated by sulfation phenomena and by electrolyte stratification effects, which can become more severe when operating at elevated charge–discharge rates [9–15]. Therefore, improving active material utilization and mitigating sulfation while preserving compatibility with the established lead–acid chemistry remains an important research objective. To overcome these challenges,

innovation in both electrode materials and electrolytes is crucial.

A promising route to address these limitations is the morphological engineering of electrodes through nanostructured architectures [16–19]. Compared with conventional pasted plates, nanostructured electrodes can increase the electrochemically active surface area and improve the accessibility of the electrolyte to the active material, which may enhance utilization of active material and reduce polarization. In addition, shorter characteristic transport lengths within the porous network can facilitate charge and mass transport, supporting operation at high charge–discharge rates and under deep-cycling conditions [20]. Previous studies have reported encouraging results with nanostructured lead dioxide and lead electrodes, including improved performance at high rates and improved cycling stability under harsh regimes [21]. These improvements have also been reported across a range of operating temperatures and in the presence of gel electrolytes, indicating that the benefits of nanostructured architectures may persist under different practical conditions [22–24]. Beyond rate capability, nanostructured

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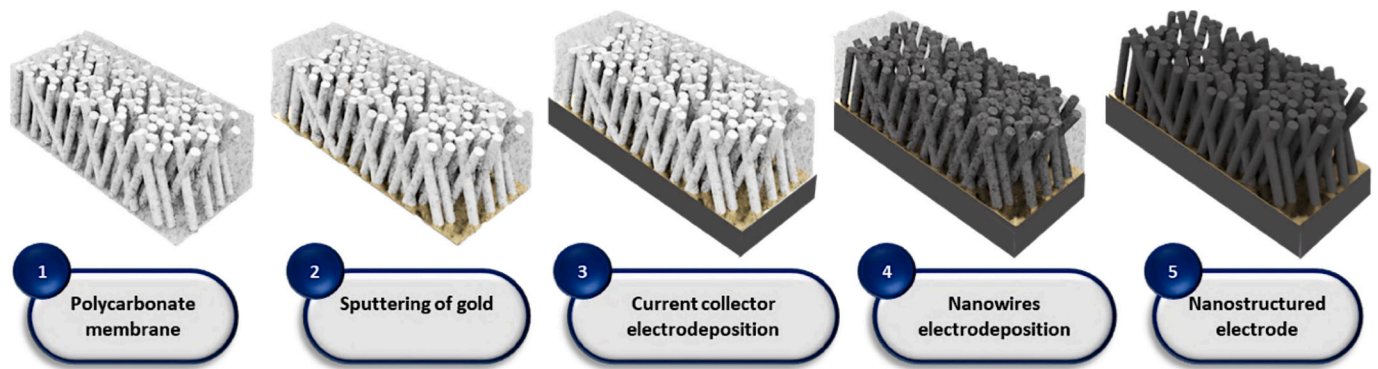


Fig. 1. Nanostructured electrode fabrication.

Table 1
Inventory for Pb electrodes.

Process	Input	Quantity
Sputtering	Polycarbonate	0.17 g
	Gold	9.6 mg
	Electricity	37.2 Wh
Electrodeposition	Lignin sulfonate	3.2 g
	Boric acid	10.8 g
	Fluoroboric acid	25.4 g
	Lead fluoroborate	29.2 g
	Graphene oxide	40 mg
	Distilled water	180 g
	Sodium acetate	1.2 g
	Acetic acid	0.4 µg
	Dichloromethane	126 mL

Table 2
Inventory for PbO₂ electrodes.

Process	Input	Quantity
Sputtering	Polycarbonate	0.17 g
	Gold	9.6 mg
	Electricity	37.2 Wh
Electrodeposition	Lead nitrate	168.9 g
	Nitric acid	9.6 g
	Chloroform	126 mL

Table 3
Assembly process.

Input	Quantity
Lead	43.2 g
Battery separator	4.9 g
Polyethylene	39.6 g
Polypropylene	429 g

architectures can influence the formation and removal of reaction products and gas bubbles at the electrode–electrolyte interface, which may contribute to more stable operation compared with dense structures. More broadly, nanostructured morphologies can enhance the performance of electrochemical devices by increasing the accessible reaction area and facilitating interfacial processes [25].

In parallel with morphology control, carbon-based additives have been widely investigated to improve the behavior of negative plates and suppress hard sulfation [26–28]. These additives can act through multiple, often concurrent effects, including changes in interfacial charge transport, modulation of lead sulfate nucleation and growth, and improved electrolyte access within the porous negative electrode. Among them, Graphene Oxide (GO) has attracted attention because it can be processed from aqueous dispersions and contains oxygen

functional groups that can influence wettability and interfacial chemistry [29–31]. Several works report that graphene- or graphene-oxide-based additives can reduce polarization, modify lead sulfate crystallization, and improve cycling stability under challenging operating conditions [32–40]. GO is a graphene derivative produced through the oxidation of graphite. Thanks to this functionalization, GO exhibits distinctive properties that differentiate it from graphene, such as high hydrophilicity (due to the oxygen groups) and high chemical reactivity, owing to the functional groups that offer reactive sites for further chemical modifications. Reduced Graphene Oxide (rGO), obtained by partially removing oxygenated groups from graphene oxide, is often associated with enhanced electronic transport while still retaining some functional groups that may support electrolyte interaction [41]. In this context, reduced graphene oxide has been investigated as an additive for negative electrodes in lead–acid batteries to improve electrochemical performance and cycle life [42–44]. Rossini et al. [44], developed nanostructured lead electrodes with reduced graphene oxide and reported improved capacity utilization and extended cycling stability, attributing the benefits to improved charge transport and more efficient utilization of the active material.

All these studies suggest that adding rGO to negative electrodes can mitigate lead sulfate formation, enhance electrical conductivity, and improve the cycling stability of batteries.

Although these studies highlight the potential of nanostructured electrodes and carbon-based additives, two gaps remain. First, demonstrations at the level of a fully nanostructured 12 V lead–acid battery operated under high-rate deep-cycling conditions are still scarce. Second, performance-oriented studies on reduced-graphene-oxide-modified nanostructured lead–acid batteries are rarely complemented by an environmental assessment based on a cradle-to-gate life cycle assessment, which is needed to quantify the contribution of the additive and identify the main impact drivers of laboratory-scale fabrication routes.

In this study, reduced graphene oxide is deposited onto nanostructured lead electrodes through an electrochemical reduction process [45], and the resulting electrodes are evaluated in a fully nanostructured 12 V battery operated at high rate and under deep discharge conditions. The performance is directly compared with a reference battery fabricated without reduced graphene oxide under the same protocol. The present study incorporates an LCA analysis on the manufacturing process, to demonstrate that the use of rGO (despite being an expensive material) still has a low impact. Life Cycle Assessment (LCA) methodology is implemented as a systematic tool to quantify and analyze the environmental impacts throughout the product life cycle, examining the contribution of rGO on the total environmental footprint. This methodology enables the early identification of critical materials and stages supporting eco-design strategies. Although the technology is currently at an early laboratory development phase, the LCA supports development during technology maturation, thereby improving its overall environmental sustainability [46].

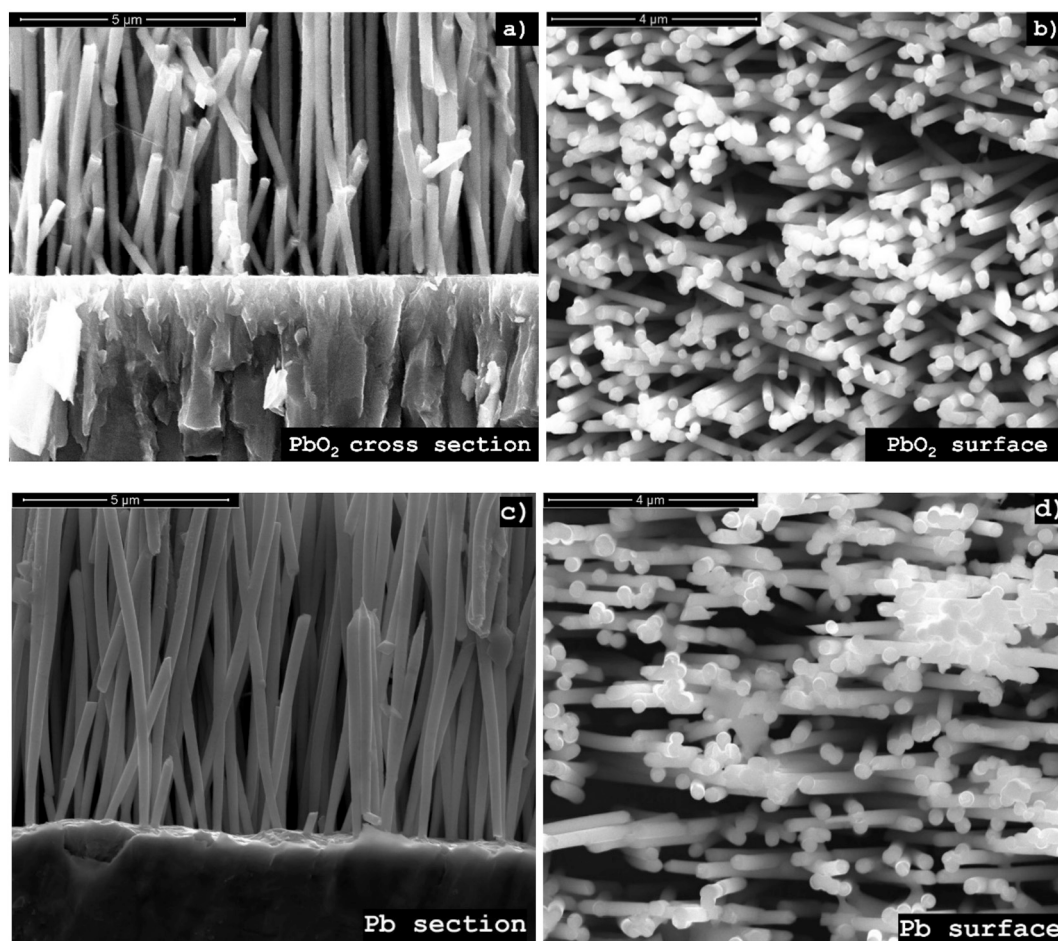


Fig. 2. SEM images of PbO_2 (a-b) and Pb (c-d) NWs after fabrication: (a) and (c) cross-section view; (b) and (d) top surface view.

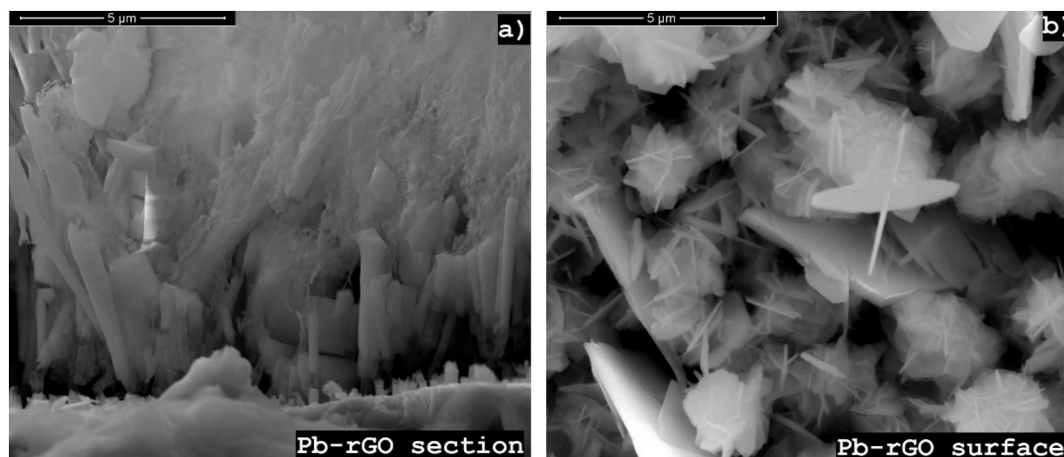


Fig. 3. SEM images of Pb NWs after GO deposition: a) cross-section view; b) top surface view.

2. Materials and methods

2.1. Electrode fabrication and characterization

Lead oxide (PbO_2) and lead (Pb) nanostructured electrodes were obtained by template-assisted electrodeposition, as reported in previous works [20]. Polycarbonate membranes of the Whatman Cyclopore 47 track-etched type, with a mean pore diameter of 200 nm and a thickness of 15 μm , were used as templates for the growth of nanostructures.

The template electrodeposition process consists of several stages. To make the membrane conductive, the first step involves sputtering of a surface using a Quorum Q300T T plus system, to quickly obtain a uniform gold film (30 nm) on the polycarbonate template, thick enough to ensure good conductivity. Following this step, a current collector of Pb or PbO_2 is deposited on the gold layer, serving both as a mechanical support for the nanostructures and as an electrical contact. Finally, the nanowires (NWs) grow inside the pores of the membrane. The deposition process, with its various steps, is illustrated in Fig. 1.

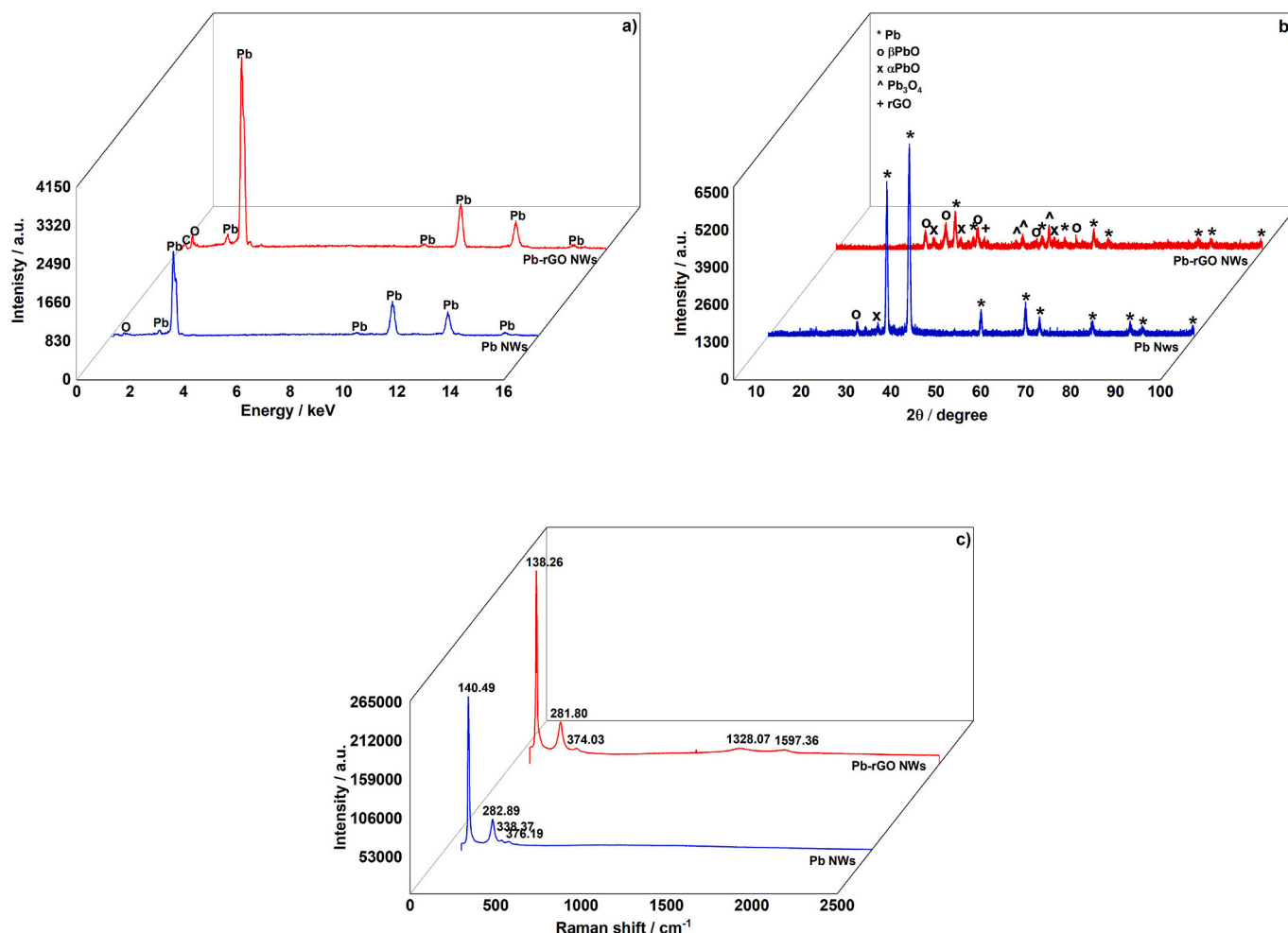


Fig. 4. Characterization of Pb electrode with and without rGO: a) EDS spectra; b) XRD patterns; c) Raman spectra.

Table 4

FT-IR analysis.

Wavenumber (cm ⁻¹)	Possible assignment
~463 - ~482	$\nu(\text{Pb}-\text{O})$ lattice modes
~521 - ~561	$\nu(\text{Pb}-\text{O})$ stretching
~650	$\nu(\text{Pb}-\text{O}-\text{Pb})$ (tetragonal lattice $\alpha\text{-PbO}$)
~680	$\nu(\text{Pb}-\text{O}-\text{Pb}) / \nu(\text{Pb}-\text{O}-\text{C})$
~1232	$\nu(\text{C}-\text{O})$ surface carbonate
~1385 - ~1395	δ bending (O-H) of adsorbed hydroxide groups and/or ν s (C-O) of surface lead carbonate (PbCO_3)
~1766	$\nu(\text{C}=\text{O})$ stretching

In case of PbO_2 electrode fabrication, the current collector is deposited at room temperature, creating a compact lead oxide layer by applying a constant current of 10 mA cm^{-2} until a charge of 80 C cm^{-2} is reached. Following this step, the nanostructures are electrodeposited inside the membrane channels by applying a constant potential of 1.5 V versus the saturated calomel electrode (SCE) until a charge of 8 C cm^{-2} is achieved. Both electrodepositions were performed using an aqueous solution of $1 \text{ M Pb}(\text{NO}_3)_2$ and 0.3 M HNO_3 . After electrodeposition, the electrode is washed and dried, and after assembly, the membrane is dissolved using chloroform.

Regarding the lead electrode, on one side of the gold-coated membrane, a compact lead layer approximately 30 nm thick is deposited. The current collector deposition is carried out in three steps, each lasting 960 s , using a pulsed current and replacing the deposition solution after

each cycle. The pulsed current shape was rectangular, with a maximum current of -10 mA cm^{-2} lasting 5 s , and a minimum current of 1 mA cm^{-2} lasting 0.25 s . After deposition, the sample was washed with distilled water, and on the other side of the membrane, nanowire deposition was performed using the same bath and pulsed current shape as for the current collector but with a deposition time of 450 s , reaching lengths of about $10 \mu\text{m}$. The deposition bath consists of a solution containing 4.5 g L^{-1} lignin sulfonate, $15 \text{ g L}^{-1} \text{H}_3\text{BO}_3$, $35.2 \text{ g L}^{-1} \text{HBF}_4$, and $40.5 \text{ g L}^{-1} \text{Pb}(\text{BF}_4)_2$. After electrodeposition, the electrode is washed and dried, and then the membrane is dissolved using dichloromethane.

The fabrication of nanostructured electrodes was performed using a PAR Potentiostat/Galvanostat (model PARSTAT MC) connected to a PC and controlled by VersaStudio® software.

For the deposition of rGO, the Pb electrode is first assembled, and then rGO is deposited using a solution containing 30 mL of a GO dispersion (4 g L^{-1}) in acetate buffer (ABS) at pH 5.4. A platinum mesh as the counter and an SCE as the reference electrode were used. The deposition lasted 600 s , with the electrode potential maintained at -0.8 V vs. SCE. The current density measured during rGO deposition is shown in Fig. S1.

Scanning electron microscopy (SEM, FEG-ESEM, FEI QUANTA 200), Raman (Renishaw, inVia Raman 158 Microscope), and electron dispersive (EDS, EDAX Ametek) spectroscopy were carried out in different areas of the electrode. The samples were also characterized by X-ray diffraction (XRD, RIGAKU D-MAX 25600 HK) and Fourier-transform infrared spectroscopy (FT-IR, Perkin-Elmer FT-IR/NIR Spectrum 400). Nanostructured electrode wettability was evaluated by contact angle

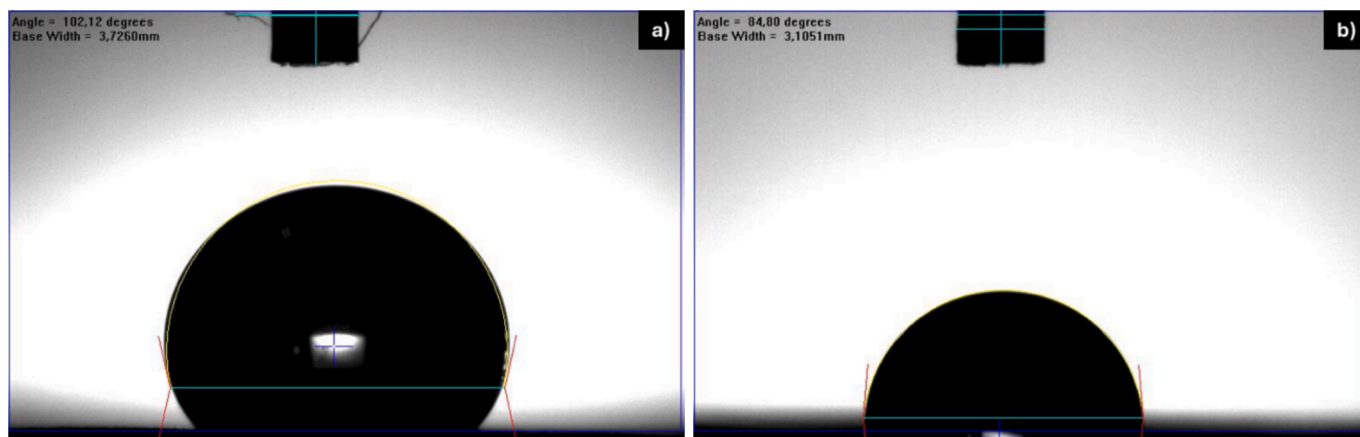


Fig. 5. Contact angle performed on the surface of Pb (a) and Pb-rGO (b) nanostructured electrodes.

measurements in a 5 M H_2SO_4 as wetting liquid, using a FTA 1000 (First Ten Ångströms) instrument. Contact angle was measured on different points of the surface to evaluate electrode uniformity.

2.2. Battery testing and assembly

The samples were tested as battery negative and positive electrodes in 5 M H_2SO_4 , using an AGM (Absorbent Glass Mat) separator in a zero-gap configuration. The 12 V battery was assembled using six different 2 V cells, each composed of three PbO_2 NW electrodes in parallel configuration (to increase the capacity) and one Pb electrode with rGO addition. Once assembled, the 12 V battery was subjected to a high C-rate, 10C, imposing a cut-off voltage of 7.2 V, and then setting a DoD (Depth of Discharge) to 90%. This value was selected so as not to exceed the conversion of the active material and allow the electrical continuity of the remaining unconverted part on the current collector during the charging process. To highlight the effect of rGO, a 12 V battery containing a Pb electrode prepared without rGO was tested under the same conditions.

The first charge of each battery was carried out stepwise, as reported in previous works [20,23], to avoid severe gas evolution and cracking of the electrode. The current was stepwise increased from C/5 to 10C, and each step delivered the same charge.

2.3. Life cycle assessment methodology

The LCA analysis was performed in accordance with the International Organization for Standardization (ISO) standard 14040 [47] and ISO 14044 [48] standards. This analysis is structured into four interrelated phases. The goal and scope definition establishes the study objectives, delineates system boundaries, and specifies the functional unit, impact categories, and assessment methodologies. The life cycle inventory involves systematic data collection and calculation to quantify resource use, emissions, and waste. The life cycle impact assessment then translates these inventory results into potential environmental impacts. Finally, the interpretation phase synthesizes the findings, providing conclusions and recommendations based on the outcomes of the preceding steps.

The specific goals studied are: (1) quantify the environmental impacts of the battery at the laboratory scale and (2) determine whether rGO produces a significant effect on the total impacts of the battery. These objectives are assessed across 16 impact categories using the environmental footprint method defined by the European standard 15804 + A2 [49]. A cradle-to-gate approach is applied, covering the stages from raw material extraction to the complete manufacturing process, defining the production of a 12 V battery as the functional unit of the analysis.

The inventory was obtained from an analysis of the laboratory-scale process and is summarized in Tables 1–3, which specify the processes, inputs, and quantities involved. A 12 V battery comprises 6 Pb electrodes and 6 PbO_2 electrodes, with each electrode undergoing three main processing steps: sputtering, electrodeposition, and a dichloromethane or chloroform bath. Subsequently, the electrodes are subjected to the assembly process. Table 1 presents the inventory related to the Pb electrodes, while Table 2 details the inventory for the PbO_2 electrodes, both referring to the production of 6 electrodes each. The inventory related to the assembly process is provided in Table 3.

3. Results and discussion

3.1. Morphological and structural characterization

The morphology of the electrodes was examined using SEM, showing that the deposition of the NWs occurred as reported in [20]. Indeed, an orderly growth of a layer of Pb and PbO_2 NWs on the surface of the current collector can be observed in Fig. 2.

Following the deposition of the nanostructures and the dissolution of the polycarbonate membrane, the Pb electrode was functionalized with rGO using the GO dispersion. The most widely accepted mechanism for the electrochemical reduction of GO to rGO is the one proposed by Dong et al. [50]:



As shown in the SEM images of Fig. 3, the initial nanowire-based morphology of the electrode has completely transformed. In the cross-section view (Fig. 3a), the NWs appear embedded and wrapped within vertically aligned, sheet-like Pb-rGO (lead added with rGO) structures, forming a compact yet highly porous framework. In the surface view (Fig. 3b), plate- and flake-shaped crystallites are uniformly distributed, further evidencing the development of a three-dimensional, open network. Despite the drastic morphological evolution, the electrode preserves a high porosity, which provides a large electroactive surface area for redox reactions during battery cycling.

To confirm the presence of rGO, further analyses were carried out. In particular, the EDS (Fig. 4a) spectra of Pb electrodes with and without rGO reveal that in the latter case, beyond the lead peaks, peaks corresponding to carbon (C) and oxygen (O) are also present.

XRD analysis (Fig. 4b) shows that in the case of the electrode with rGO, the main peaks correspond to Pb, but the presence of C is also detected. This result was obtained by processing data using Profex software. Moreover, the Raman spectra (Fig. 4c) show bands around 140, 280, and 376 cm^{-1} , which, according to the database [51], are attributed to PbO (known as litharge), while the bands around 370 cm^{-1} correspond to the orthorhombic phase of PbO (known as massicot). In

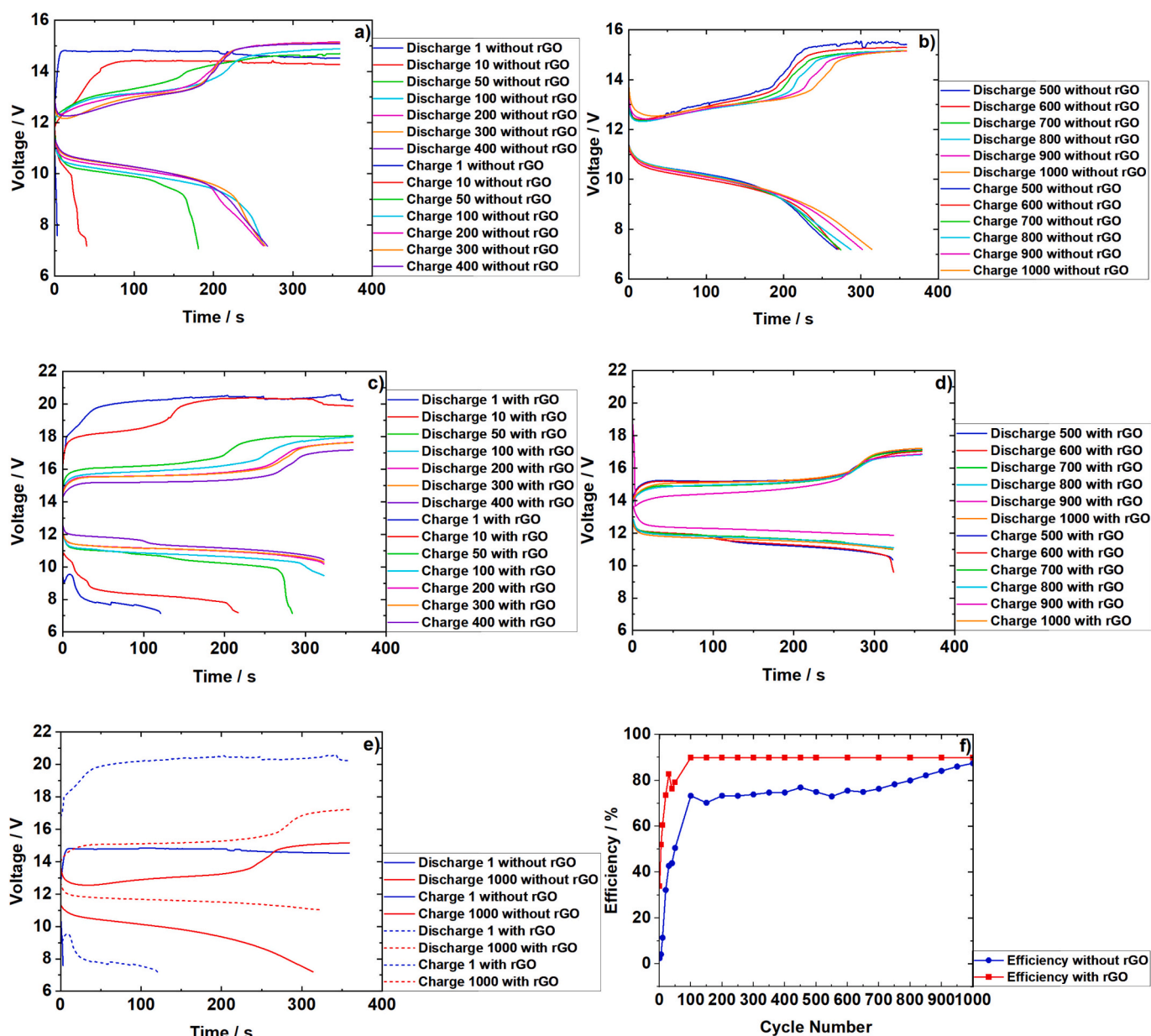


Fig. 6. Performance of nanostructured 12 V batteries: a-b) Charge/discharge curves of the nanostructured battery without rGO; c-d) Charge/discharge curves of the nanostructured battery with rGO; e) Comparison of some charge/discharge curves of nanostructured batteries with and without rGO; f) Comparison of efficiency curves of batteries with and without rGO.

the case of the electrode with the rGO, the latter was identified by isolating the Raman modes at 1328.07 and 1597.36 cm^{-1} , which clearly indicate the presence of rGO on the surface of the lead electrode. In particular, the Raman features at 1328.07 and 1597.36 cm^{-1} assigned to the D band (approximately $1300\text{--}1400\text{ cm}^{-1}$) and the G band (approximately $1580\text{--}1605\text{ cm}^{-1}$), are commonly associated with disordered and graphitic carbon frameworks in reduced graphene oxide materials. The degree of disorder and reduction was assessed by evaluating the intensity ratio between the D and G bands (I_D/I_G). The I_D/I_G value close to 1 (1.09) indicates a high degree of disorder, which is typical of a partially reduced material that may retain oxygen-containing functional groups obtained by electrochemical reduction [52]. Thus, Raman spectroscopy supports the formation of an electrochemically reduced graphene oxide layer on the lead electrode surface.

A further analysis was carried out on the samples involving Fourier-transform infrared spectroscopy (FT-IR, Fig. S2). The identification of FT-IR spectra of Pb and Pb-rGO electrodes is reported in Table 4.

In the lead nanostructured electrodes, the presence of peaks related to PbO may be because the electrode was exposed to air for several days before the analysis, leading to natural surface oxidation.

Wettability study of the surface of Pb and Pb-rGO electrodes was also carried out to verify whether the presence of rGO in the electrode had influenced this parameter (Fig. 5).

In the case of the electrode containing rGO, there is greater wettability of the electrode surface. The contact angle changes from approximately 102° (Pb electrode) to approximately 85° (Pb-rGO electrode), indicating improved hydrophilicity due to the oxygen-containing functional groups in rGO.

The same analyses were also performed on the PbO₂ electrodes. In particular, the EDS spectra (Fig. S3) show only the peaks corresponding to oxygen and lead, and the XRD analysis (Fig. S4) shows the presence of peaks corresponding exclusively to β -PbO₂. FT-IR analysis (Fig. S5, Table S1)) shows that the highest absorbance ($432\text{--}642\text{ cm}^{-1}$) confirms a significant presence of PbO₂ [53], and the Raman spectra (Fig. S6)

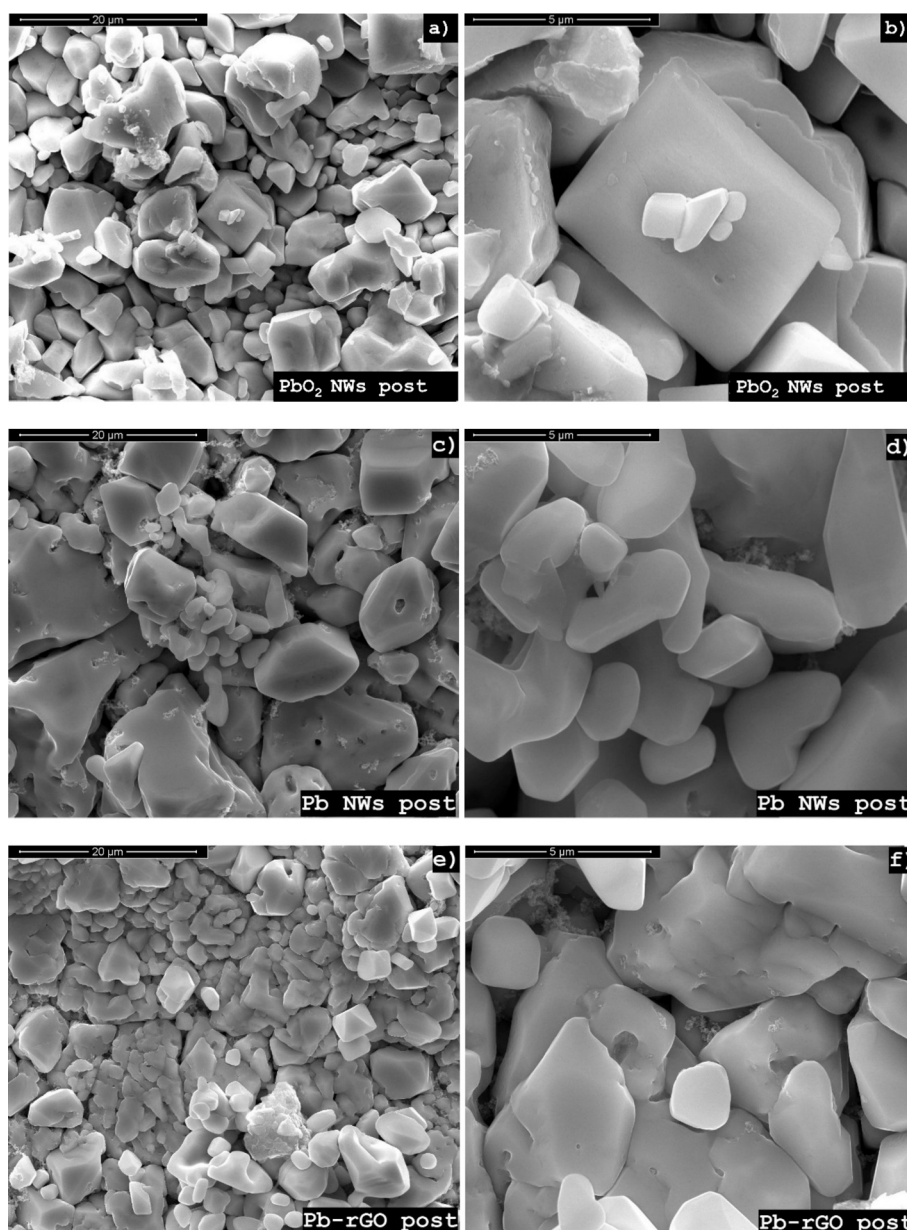


Fig. 7. SEM images of nanostructured electrodes after cyclization at different magnifications: a-b) PbO_2 NWs electrode; c-d) Pb NWs electrode; e-f) Pb-rGO electrode.

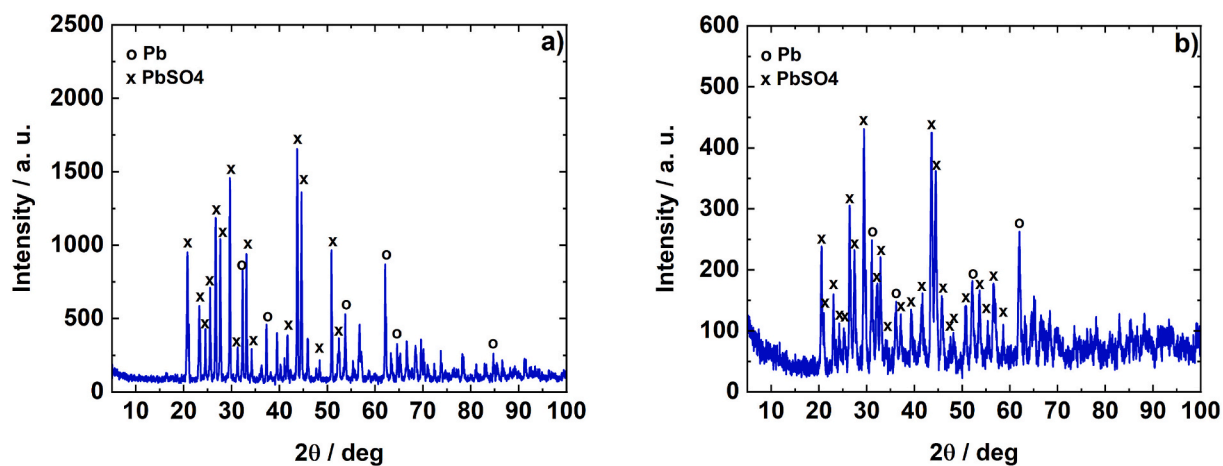


Fig. 8. XRD patterns of the lead electrode (a) and Pb-rGO electrode (b) after cyclization.

Table 5

LCA results for the battery.

Impact categories	Unit	Total
Acidification	mol H ⁺ eq	3.68E-02
Climate change	kg CO ₂ eq	5.57E+00
Freshwater ecotoxicity	CTUe	1.49E+02
Particulate matter	disease inc.	3.94E-07
Marine eutrophication	kg N eq	5.98E-03
Freshwater eutrophication	kg P eq	3.83E-03
Terrestrial eutrophication	mol N eq	6.78E-02
Human toxicity (carcinogenic effects)	CTUh	2.20E-08
Human toxicity (non-carcinogenic effects)	CTUh	2.38E-07
Ionising radiation	kBq U-235 eq	3.05E-01
Land use	Pt	1.75E+01
Ozone depletion	kg CFC11 eq	2.85E-04
Photochemical ozone formation	kg NMVOC eq	2.26E-02
Fossils resource use	MJ	8.25E+01
Minerals and metals resource use	kg Sb eq	1.37E-03
Water use	m ³ depriv.	1.40E+00

exhibit bands around 138, 230, 332, and 520 cm⁻¹, confirming the presence of β-PbO₂ [54,55].

3.2. Battery performance under cycling

The nanostructured electrodes were assembled into a 12 V battery in a zero-gap configuration. The characteristic charge-discharge curves of the tested batteries are shown in the Figs. 6.

In both cases, with and without rGO, the nanostructured batteries exhibit an increase in usable energy during the charge/discharge process. In addition, a complete absence of spikes in the discharge curves can be observed. This indicates there is no significant gas generation at the electrodes, which could otherwise lead to battery failure. Specifically, for the nanostructured batteries containing lead electrodes enhanced with rGO, a higher potential is noticeable during both charge and discharge phases compared to batteries without rGO. This behavior is likely due to the presence of rGO, which enables greater charge storage on the electrode surfaces due to its high surface area and conductivity.

Furthermore, as shown by the efficiency curve comparison, the maximum efficiency value of 90% is reached by the rGO-containing batteries only after approximately 100 charge-discharge cycles, and this level is maintained consistently throughout the duration of the test. In contrast, batteries without rGO show lower efficiency values and

reach the 90% efficiency threshold more slowly, if at all, during the testing period. Specific energy density at representative cycle numbers for both configurations is summarized in Table S4. The presence of rGO increases the specific energy density of about 17% (value calculate after battery stabilization). As can be observed, both configurations exhibit higher specific energy density values than those of commercial lead acid battery (typical in the range 20–40 Wh/Kg). In addition, galvanostatic electrochemical impedance spectroscopy (GEIS) results under load are provided in Fig. S11. These curves clearly show that the presence of rGO decreases the overall resistance of the electrode.

3.3. Post-cycling morphological and compositional analysis

After cycling, the electrodes were characterized by SEM, EDS, XRD, FT-IR, and Raman analyses to assess their updated morphology and composition.

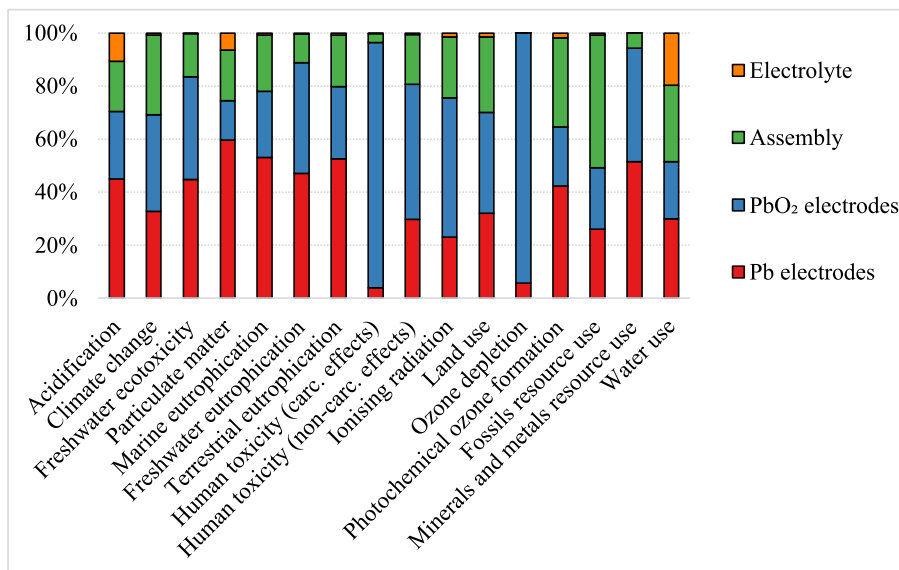
The SEM images, Fig. 7, of the electrodes after 1000 cycles, show the formation of a similar morphology in all cases, characterized mainly by the presence of lead sulfate crystals. However, the structure remains porous, indicating that the electrodes still have the potential to undergo further charge-discharge cycles and that sulfation was not the limiting factor for the cycle life of nanostructured batteries.

The EDS spectra of the electrodes after cycling show (Fig. S7), in addition to the peak related to sulfate, also the peaks corresponding to lead and carbon in the case of the electrode with rGO additive (Fig. S7b), confirming that rGO remained on the electrode surface throughout the cycling process.

In addition, as shown by the XRD spectra (Fig. 8a) of the Pb and Pb-rGO electrodes after cycling, both electrodes consistently show the presence of unconverted active material, confirming the hypothesis that the battery could have continued to operate for additional charge-discharge cycles. The XRD spectrum of PbO₂ electrode after cyclization shows the same behavior, demonstrating that the active material was not completely converted even after 1000 cycles (Fig. S8).

To provide a quantitative comparison between the post-cycling Pb and Pb-rGO electrodes, the XRD pattern was used to calculate the average crystallite size that was estimated using the Scherrer's equation from the full width at half maximum of the main diffraction peaks relative to the lead sulfate phase:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

**Fig. 9.** Contribution analysis for the battery.

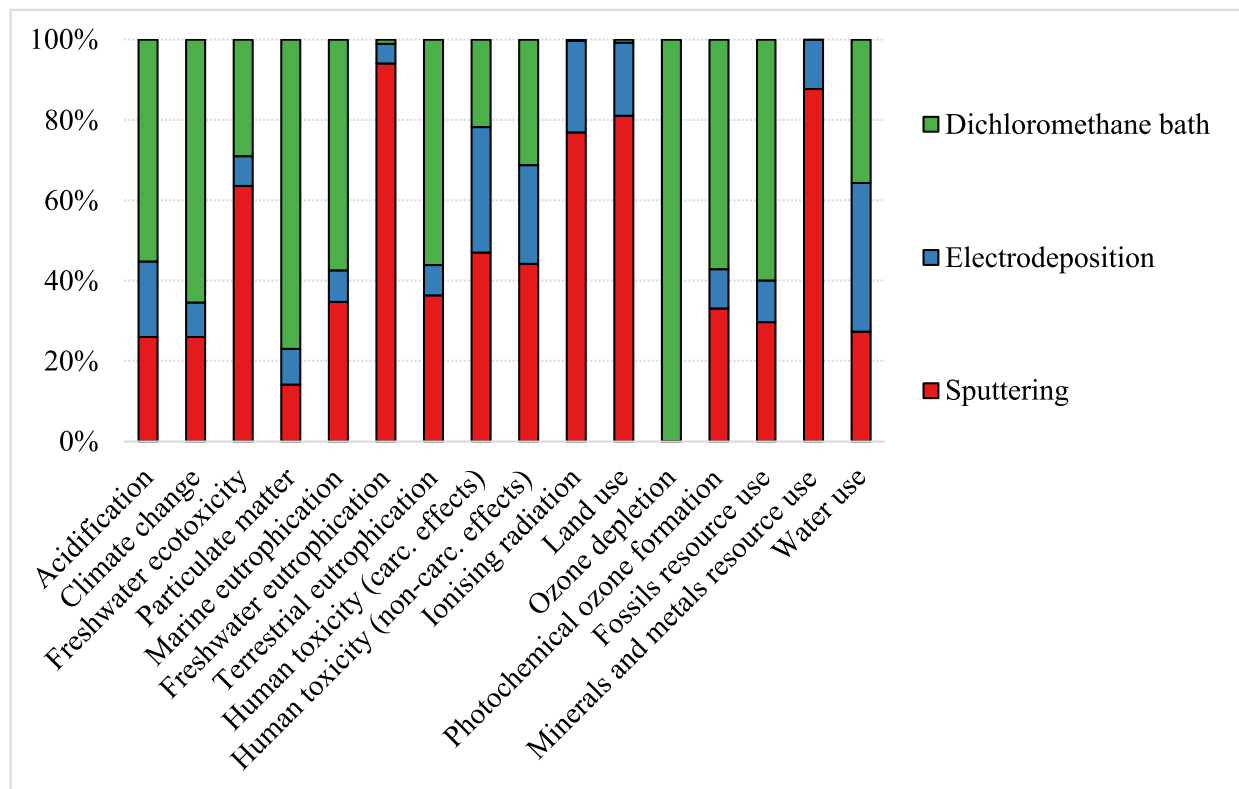


Fig. 10. Contribution analysis for the Pb electrodes.

Table 6

Results for the Pb electrodeposition, highlighting rGO incidence.

Impact categories	Unit	Total	rGO incidence
Acidification	mol H ⁺ eq	1.56E-03	2.5%
Climate change	kg CO ₂ eq	7.82E-02	6.0%
Freshwater ecotoxicity	CTUe	2.44E+00	3.1%
Particulate matter	disease inc.	1.03E-08	2.6%
Marine eutrophication	kg N eq	1.25E-04	3.7%
Freshwater eutrophication	kg P eq	4.40E-05	5.3%
Terrestrial eutrophication	mol N eq	1.35E-03	3.0%
Human toxicity (carcinogenic effects)	CTUh	1.37E-10	9.9%
Human toxicity (non-carcinogenic effects)	CTUh	8.59E-09	0.7%
Ionising radiation	kBq U-235 eq	8.01E-03	10.3%
Land use	Pt	5.02E-01	3.6%
Ozone depletion	kg CFC11 eq	2.00E-09	29.8%
Photochemical ozone formation	kg NMVOC eq	4.69E-04	3.2%
Fossils resource use	MJ	1.11E+00	6.9%
Minerals and metals resource use	kg Sb eq	4.32E-05	0.2%
Water use	m ³ depriv.	7.73E-02	5.2%

where D is the crystallite size, K is the shape factor, here assumed equal to 0.90, λ is the Cu K α radiation wavelength, equal to 1.5406 Å, β is the full width at half maximum of the selected peak expressed in radians, and θ is the Bragg angle. For this analysis the high intensity diffraction peaks of lead sulphate were selected and in particular the peaks at around 29.65°, 43.73° and 44.5°. The lead sulphate present in the post-cycling Pb electrode has an average crystallite size of 27.66 ± 0.89 nm. In contrast, the lead sulphate of Pb-rGO electrode showed a lower average crystallite size of 17.28 ± 0.85 nm. Thus, the incorporation of rGO produced a reduction of approximately 38% in the mean crystallite size.

These results provide quantitative support for the SEM observations. Although PbSO₄ formation occurs on both electrodes after cycling, as confirmed by XRD, the Pb-rGO electrode is characterized by smaller crystalline grains and a narrower size distribution. This suggests that rGO limits the growth and coarsening of larger PbSO₄ crystallites. This behavior is consistent with the improved cycling performance of the rGO-containing battery, since smaller sulfate domains are generally more easily reconverted during charging and are less likely to induce irreversible hard sulfation.

The FT-IR spectra (Fig. S9, Table S2) after cyclization are very similar to each other, and the possible assignments show the presence of PbSO₄ (lead sulfate) on all three electrodes. The Raman spectra (Fig. S10) show bands in the region between 438 and 1158 cm⁻¹, which, according to the literature [48,54], are attributable to PbSO₄, while the bands around 132–142 cm⁻¹ are attributed to the tetragonal phase of PbO. In the case of the post-cycling PbO₂ electrode, there is also a peak around 514 cm⁻¹, which is attributable to the presence of PbO₂ itself. The rGO bands are not visible due to their low Raman shift, which is masked by the intense peaks of the sulfate crystals.

3.4. Life cycle assessment results

Comprehensive LCA is an effective method for detecting all hidden environmental impacts, thereby identifying areas for improvement and preventing burden shifting. The LCA results, expressed across 16 impact categories following the EN 15804 + A2 method, are presented in Table 5.

The contribution analysis (Fig. 9) indicates that the electrodes represent the primary environmental hotspots within the battery system. Specifically, Pb electrodes contribute substantially to resource use impacts, with values ranging from 4% for the human toxicity (carc. effects) category up to 60% for particulate matter. PbO₂ electrodes also exhibit notable burdens, spanning from 15% for particulate matter to a peak of 94% for ozone depletion. Similarly, the assembly process shows

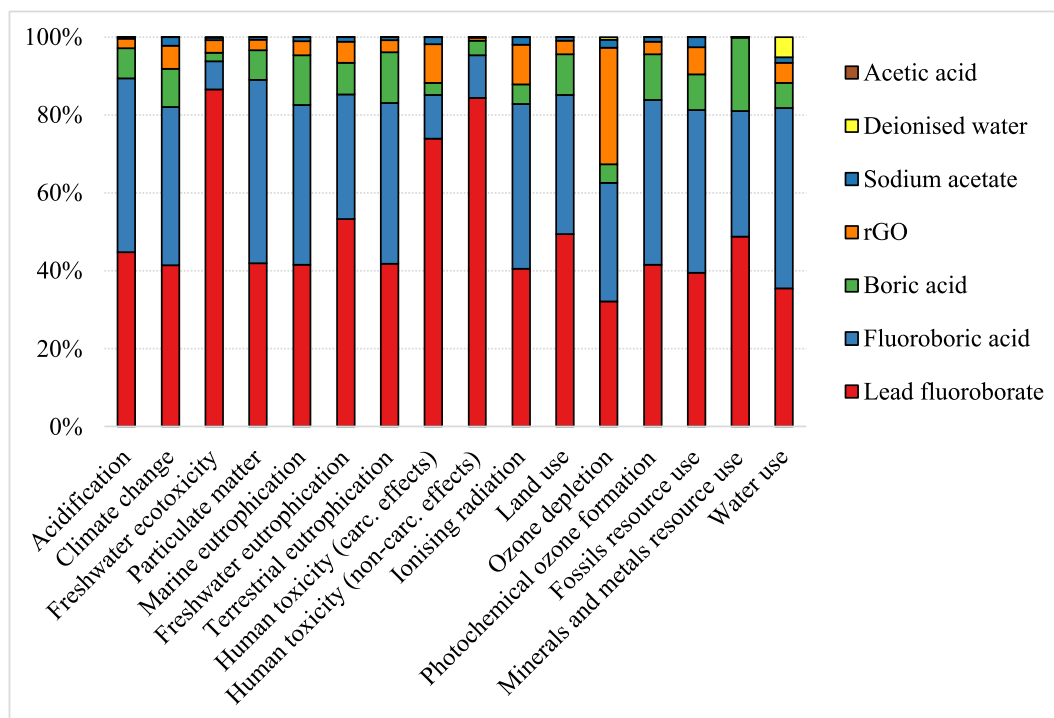
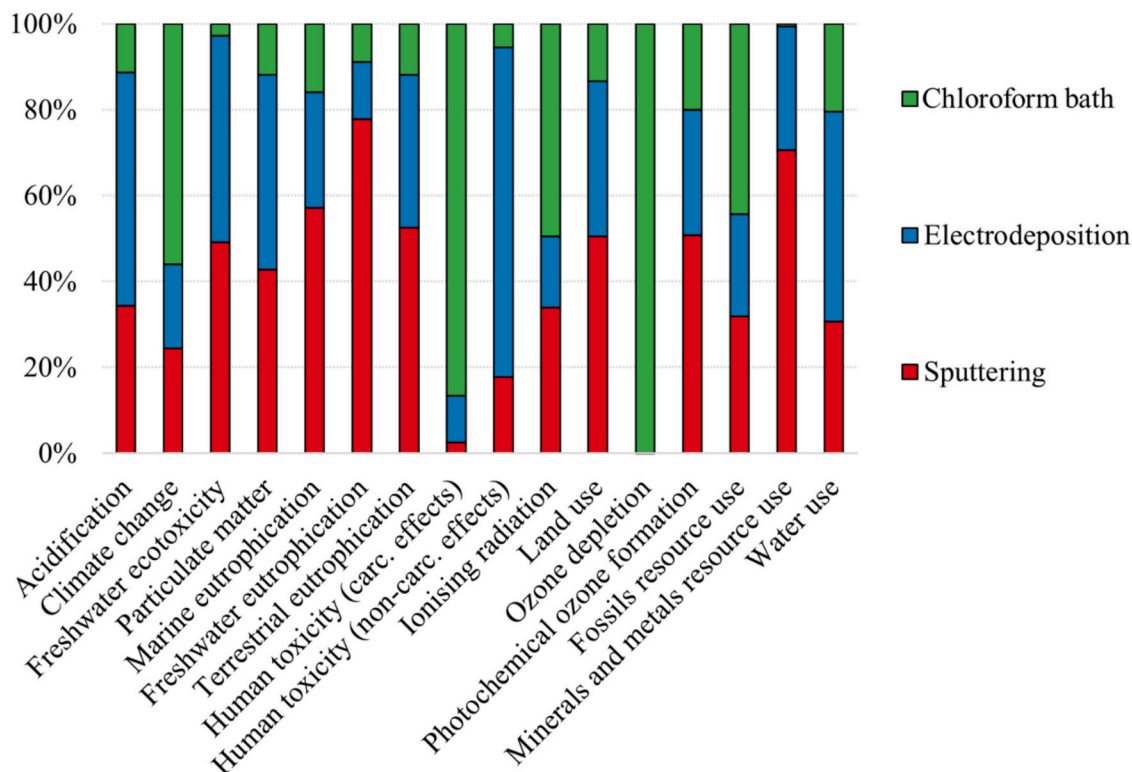


Fig. 11. Contribution analysis for the Pb electrodeposition.

Fig. 12. Contribution analysis for PbO₂ electrodes.

a highly variable contribution, from a negligible impact (close to 0%) for ozone depletion to a maximum of 50% for fossil resource use. In contrast, the electrolyte reveals generally minor contributions across most impact categories, with its highest share of 20% registered for water use.

For the Pb electrodes specifically (Fig. 10), the dichloromethane bath

stage emerges as the most critical contributor to the environmental impacts associated with electrode production. This process dominates 8 impact categories, with its contribution ranging from almost 0% to around 99.9%. The sputtering also exhibits considerable impact, accounting for 0.03% to 94% for 7 categories. Meanwhile, electrodeposition presents a moderate yet relevant effect, contributing between close

to 0% and 37%, depending on the specific impact category.

Table 6 presents the results for the Pb electrodeposition, including the rGO incidence percentage, to evaluate the impact of adding this material on the environmental performance of the system. The rGO incidence varies from 0.2% (for minerals and metals resource use) to 30% (only for ozone depletion), with an average contribution of approximately 6%. This suggests that the addition of rGO has a limited effect on the overall environmental impact of the electrode despite the significant performance improvements.

Regarding the electrodeposition stage of Pb electrodes (**Fig. 11**), lead fluoroborate emerges as the main environmental hotspot for 11 impact categories, contributing between 32% and 87%, followed by fluoroboric acid, which causes the highest impact for 5 categories varying from 7% to 47%, and boric acid, which ranges from 2% to 19%. The remaining components contribute less than 5% for almost all impact categories.

For the PbO₂ electrodes (**Fig. 12**), the sputtering stage is the main environmental hotspot in electrode manufacturing. This process is the primary contributor for 7 of the 16 considered impact categories, with its impact ranging from nearly 0% to 78%. Similarly, the chloroform bath accounts for the highest impact in 5 categories, with its contribution ranging from approximately 1% to 100%. The electrodeposition process also represents a significant contributor to several impact categories for PbO₂ electrode production.

The LCA analysis yielded truly interesting results, demonstrating that the use of rGO significantly boosts battery performance without increasing the overall environmental impact of the manufacturing process. Moreover, it enabled the identification of the most impactful stages in electrode fabrication, namely, the sputtering phase and the dissolution phase in the two solvents (dichloromethane for Pb electrodes and chloroform for PbO₂ electrodes). This outcome is particularly valuable as it highlights potential improvement actions to limit process impact: for sputtering, gold could be replaced with a cheaper material or the entire process substituted with a simple electroless Pb deposition; for solvents, which are unavoidable, a recovery process via low-temperature evaporation and recondensation (leveraging their high vapor pressure) could be implemented, allowing reuse of the pure solvent and recovery of polycarbonate.

4. Conclusions

The nanostructured lead electrodes enhanced with rGO additives demonstrated excellent performance under extreme operating conditions (10C C-rate, 90% depth of discharge), maintaining approximately 90% electrochemical efficiency over more than 1000 charge-discharge cycles. This superior performance can be attributed to the enhanced electrical conductivity and interfacial properties provided by rGO, which reduce the coarsening of PbSO₄ crystalline domains after cycling, as shown by the lower crystallite size obtained from XRD analysis. In addition, the improved surface wettability observed for the reduced-graphene-oxide-containing electrode may facilitate electrolyte infiltration and ionic transport within the porous structure, reducing local transport limitations and contributing to higher utilization of active material under high-rate cycling.

Post-cycling characterization via SEM, XRD, FT-IR, and Raman spectroscopy revealed that despite the complete morphological transformation, the electrode structure remained highly porous, and importantly, not all active material had been completely converted to sulfate. This indicates that the battery had the potential to continue operating for additional cycles, suggesting that factors other than simple sulfation may limit long-term performance in practical applications.

The LCA analysis identified sputtering and chemical baths (dichloromethane for Pb electrodes, chloroform for PbO₂ electrodes) as the primary environmental hotspots in electrode manufacturing. However, the analysis conclusively demonstrated that rGO, despite contributing significantly to performance improvements, adds only a minimal environmental burden to the overall battery system, with an average

contribution of approximately 6% across all impact categories. This finding strongly supports the viability of rGO-enhanced batteries from both performance and sustainability perspectives.

These results establish rGO-modified nanostructured lead-acid batteries as a promising technology for high-rate energy storage applications, offering an environmentally responsible path toward improved battery performance. Future research directions should focus on long-term cycling stability, scalability from laboratory to industrial production scales, and mechanistic investigations into the role of rGO in suppressing sulfate formation and enhancing active material utilization. In addition, a comparative LCA will be conducted once the technology undergoes scale-up, enabling a robust comparison of environmental impacts between the proposed NWs system and commercially mature technologies under comparable technological maturity and functional conditions.

CRedit authorship contribution statement

Maria Grazia Insinga: Writing – original draft, Formal analysis, Data curation, Conceptualization. **Alberto Affranchi:** Validation, Formal analysis. **Roberto Luigi Oliveri:** Writing – review & editing, Supervision, Methodology, Investigation. **Bernardo Patella:** Validation, Supervision, Methodology. **Giuseppe Aiello:** Validation, Supervision. **Nadia Moukri:** Supervision, Formal analysis, Data curation. **Sonia Longo:** Writing – review & editing, Validation, Supervision, Investigation. **Maurizio Cellura:** Validation, Supervision. **Rosalinda Inguanta:** Writing – review & editing, Validation, Supervision, Formal analysis, Data curation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Roberto Luigi Oliveri, Maria Grazia Insinga, Alberto Affranchi report that financial support was provided by SAMOTHRACE Foundation. Roberto Luigi Oliveri, Maria Grazia Insinga, Alberto Affranchi reports a relationship with Samothrace Foundation that includes: funding grants. No other activities are declared. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.est.2026.124550>.

Data availability

Data will be made available on request.

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