Enhancement of the Electrochemical Properties of PbO₂ by Incorporation of Graphene Exfoliated

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ABSTRACT: *Graphene (Gr) synthesized by electrochemical exfoliation method has been used to prepare the composite material (PbO₂-Gr) including different amounts of graphene (1 and 5%). Taking into account the advantages of the high conductivity of Gr and the capacitance of PbO₂, as a reference, the PbO₂-Gr composite material served for the application in lead-acid batteries as a positive electrode. On one hand, the morphology and structure of the whole pure graphene, PbO₂, and PbO₂-Gr were characterized by different technics XRD, TEM, and electrical conductivity. The electrochemical performance was evaluated by electrochemical impedance spectroscopy (EIS), cyclic voltammetry, and galvanostatic discharge tests. The discharge capacity of the PbO₂ material experienced is around 40mAh which witnessed an increase of 53mAh regarding the composite material PbO₂-Gr1%.*

KEYWORDS: *Graphene, PbO₂; Composite material; Discharge capacity; Lead-acid battery.*

INTRODUCTION

In recent years, increased demand for energy resources, storage of energy attracted a huge research attentiontoward solving the energy problemdue to their important demand in the sector of portable devices and the development prospects of the electric vehicle [1,2], it is necessary to continue research programs on the lead-acid accumulator that is the first invented rechargeable accumulator [3-5]. The main advantage of this battery is its low cost. Indeed, its manufacture made from lead, a raw material still inexpensive, is generally well controlled and its cost is therefore limited. On the other hand, lead-acid batteries are heavy and do not support deep discharges and still suffer from low mass energy and short life [6].

The most sensitive element of the lead-acid batteryis usually the positive electrode [3] and the rate of use of the positive active material in this electrode controls the battery capacity. Its gradual degradation during cycling is also often the cause of a loss of premature capacity.

Generally, the use of porous additives in the positive electrodes aims to promote the diffusion of the electrolyte [7,8] within the material itself and the use of conductivity additives tends to optimize the conduction networks of

the active materials[9,2]. Graphene is one of the additives that has good electrical conductivity and porosity [10,11].

The affinity of graphene oxide nano-sheets and lead dioxide increased electrical and ionic permeability, *via* increased charge transfer and effective adsorptive surface areafor tuning its behaviour in energy materials as an electro-catalyst, in a scalable and cost-effective way [12].

In this present work we are add a graphene in active material (PbO_2) with two percentages (1and5 %) for the improvement the capacity of the positive electrode of the lead acid battery.

EXPERIMENTAL SECTION
Experimental

The (3PbO, $PbSO_4$, H_2O) powder (3BS) was mixed with water and 1.4 M H_2SO_4. The formation of the mixture was achieved by the employment of a tubular electrode. A lead rod is embedded in the tubular electrode serving as an electronic conductor. This rod ensures the contact between the spine and 3BS and initiates its conversion to PbO_2. The electrode is formed in 1.05 M H_2SO_4 solution. The electrode was polarized at a constant current of 10 mA until the complete mass of 3BS is totally converted to a brownish-black PbO_2 powder.

The sample was washed with a hot saturated ammonium acetate solution to remove $PbSO_4$, then washed with distilled water and overnight dried at 60°C [7].

Synthesis of Graphene

Graphene is synthesized through electrochemical exfoliation. Two high-purity graphite rods set parallel at 6cm from each other in ionic solution of 2.6 mL of sulphuric acid in 100 mL deionised water. The electrochemical exfoliation is performed in different potential between the graphite electrodes (5 V for 5 minutes). Furthermore, the graphene sheet suspension is prepared so that the exfoliated graphene sheets are collected on a 100 nm porous filter and washed under vacuum filtration with deionised water then 5 minutes dried and dispersed in N, N-dimethylformamide (DMF) solution by mild water-bath sonication for 5 minutes. The suspension thus obtained was submitted to centrifugation at 2500 rpm in order to eliminate unwanted large graphite particles. The final purified suspension is hence ready to be characterized and serve to film production. The whole electrochemical exfoliation processes were performed at normal room-temperature [13].

Characterization

The PbO_2 and Graphene were examined through diverse technical methods. For their parts, the X-ray analysis examination was carried out the Rigaku make powder X-ray diffract meter (model RINT 2100) with a CuKα waves (λ = 1.54 Å), the electrical conductivity of the samples was measured using a Kheithley 2400 electrometer with LUCAS LABS Model (PR04-8400).

Electrochemical tests

The following electrochemical tests were carried out at normal environment temperature inside a single compartment cell using, as usual, the PGZ-301 Voltalab connected to a computer with operating software (voltamaster 4). The latter enables the electrochemical technique selection and establishes the aimed parameters. The measurements at electrochemical scale were operated in a three-electrode cell where material active acted as working electrode, the Saturated Calomel Electrode (SCE) as a reference electrode and the graphite rod as an auxiliary electrode.

RESULTS AND DISCUSSION

The TEM images of the exfoliated graphene sheet in supercritical acetone are shown in Fig. 1. It is evident that the relative transparency is due to the conversion of the graphite into a few layers of graphene [14].

The Fig. 2 shows the XRD of graphite and graphene samples. So, the XRD graphite powder sample (Fig. 2A) points up the characteristics peaks of (002) at 26.50°, (010) at 42.31° and (004) at 54.60° with high intensity [13,15]. The graphene powder (Fig. 2B) designates a characteristic peak of (002) at 26.60° with weaker peak compared to the graphite one's. The noticed intensitydecreases of (002) plan peak suggests the large exfoliation of graphite to graphenenanosheets [13, 16].The size of graphene nanoparticles evaluationisquantifiedby the XRD in applying Debye–Scherrer's formula:

$$D = 0.9\lambda / w \, Cos\theta \qquad (1)$$

While,D the size of nanoparticle, λ the XRD wavelength, wthe full-width half maxima and$\theta$is the peak position. The size of graphene-nanoparticles formula evaluation is around 13 nm.
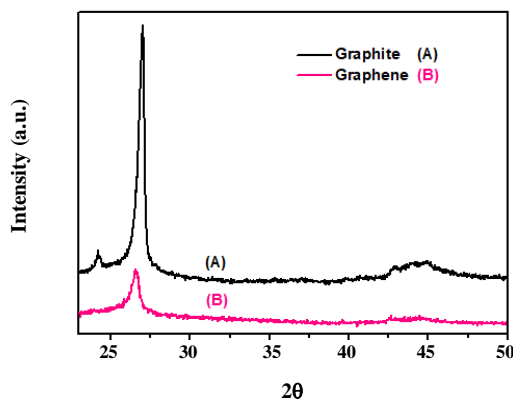
Fig. 1: TEM image of graphene exfoliated in acetone.

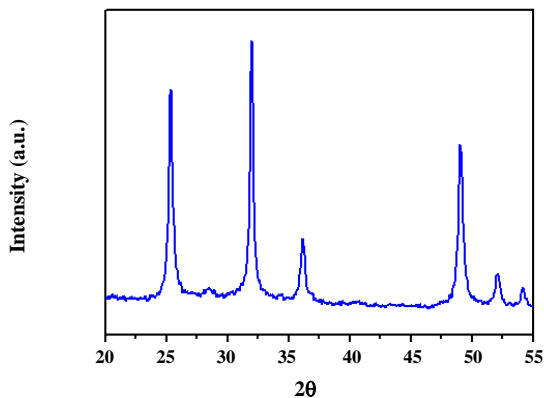**Fig. 2: XRD spectra of natural graphite (A) and graphene (B).**

Fig. 3: XRD spectra of PbO₂ Powder prepared.

Fig. 3 shows the X-ray diffraction pattern of the obtained oxide (PbO_2) by oxidation of the ($PbSO_4$, PbO, H_2O). The spectrum study shows that the lines of this spectrum are perfectly indexed with those given

by A.S.T.M (No. 11-541) and (No. 25-447) sheets respectively of β $PbO_2$with different intensities [7].

From the spectra of X-R we can calculate the grain size using SHERRER formula (1). The calculation of the particle size of β PbO_2 is based on the measurement of the center and the diffraction peak half-height width of the main line $2\theta = 25.42$. The grain size of $\beta PbO_2 = 50.2$ nm.

The electrical conductivity of PbO_2 and PbO_2-Gr active materials (1%, 5%) measured is reported in Table 1. Systematically, the electrical conductivity of PbO_2 increases with the addition of graphene in the active materials. The electrical conductivity reaches the value of 53.5 S/cm for PbO_2-Gr 1% which is twice as high as the conductivity of PbO_2 alone 25.2 S/cm. The increase in electrical conductivity observed is probably due to the nanometric dispersion of graphenenanosheets in the active material with formation of a conductive matrix. We noticed an increase in the composite material (PbO_2-Gr) conductivity following the 1% addition of the graphene in the PbO_2. The increase could be attributed to the presence of the graphene that facilitates the diffusion of the electrolyte through the positive active material (PbO_2). Once the graphene addition is more than 1%, the (PbO_2-Gr) conductivity decreases. It seems that the graphene addition in the PbO_2 at more than 1%, parts of the PbO_2 are isolated from each other and obviously the electronic conductivity of the (PbO_2-Gr) is negatively affected. This explains the progressive decrease in conductivity for the 5% graphene.

The cyclic voltammetry is being the adequate method to characterize the materials capacitive performance. The Fig. 4 show the cyclic voltammograms of PbO_2 and PbO_2-Gr (1 and 5wt%) composite materials led in a potential scale of 0 to 1.2 V vs.SCE with scan rates 50 mV/s.

Thus, the specific capacitance is accurately evaluated from the following equation (2):

$$SC = \frac{\int_{E_1}^{E_2} i(E)\,dE}{2(E_2 - E_1)\,m\,v} \quad (2)$$

SC: Specific capacitance

E_2-E_1: Potential window in cyclic voltammetry

$\int_{E_1}^{E_2} i(E)dE$: Voltammetric charge obtained by integration of curve in CV.

m: weight of deposited materiel on working electrode, we used a balance with accuracy of 0.01 mg

v: Scan rate.

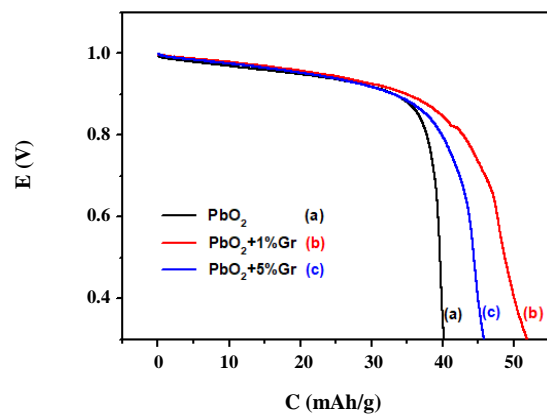***Table 1: Values of electrical resistivity and electrical conductivity of PbO₂ and PbO₂-Gr (1% and 5%).***

	PbO$_2$	PbO$_2$+1%Gr	PbO$_2$+5%Gr
Electricalresistivity (Ohm.cm^2)	0.039	0.019	0.018
Electricalconductivity (S/cm)	25.2	53.5	52.3
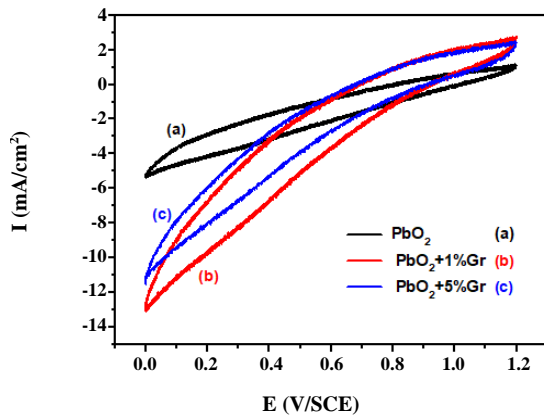
Fig. 4: Cyclic voltammograms of PbO₂ and PbO₂-Gr powders (1%, 5%) at a scanning rate of 50 mV/s, in 1.28 M H₂SO₄ electrolyte.

Fig. 5: Discharge curves and capacities of PbO₂ with various graphene contents.

First, in compared to the PbO$_2$ powder, the wholePbO$_2$-Gr witnesses an obvious increase in the areas charge-discharge curves cyclic voltammetry plots,this is due totheGraphene mass incorporated in active material. Second, the cyclic plots points up to a reversible Red/Ox response as expected on the basis of the theoretical principles related to the scientific issue background. PbO$_2$ shows a specific capacity of about 50.49 F/g at 10 mV/s. After incorporation of graphene, we observed a significant increase in specific capacity which was 85.55 F/g and 112.92 F/g for the composite materials PbO$_2$-Gr 5% and PbO$_2$-Gr 1% respectively.Taking into account the figures issued from our experimentation, we clearly notice an increase in specific capacitance resulting from the graphene addition in PbO$_2$ mass. In fact, the best increase in specific capacitance took place after 1% graphene inclusion in PbO$_2$ mass – in number term i.e. from 50.49 F/g to 112.92 F/g. Such increase often ascribed to the subsequent electrode conductivity augmentation.

To see the performance of PbO$_2$ and the graphene added on the discharge capacity of PbO$_2$, we plotted potential variation curves as a function of the discharge capacity, the latter is calculated from the following Eq. (3):

$$C = \frac{I \times t}{m} \quad (3)$$

I: imposed current (mA).

t: Time of discharge (h).

m: mass of lead dioxide used in the discharge (g).

Fig. 5 shows the curves of potential variation versus discharge capacity of PbO$_2$ alone and PbO$_2$ contains different amount of graphene. From these curves, it can be seen that each electrode has a landinglocated around 1V vs SCE, corresponding to the reduction reaction of PbO$_2$ to PbSO$_4$ followed by a sudden total drop during discharges. Note that the capacity of PbO$_2$ is dependent on the amount of graphene added to PbO$_2$.

It is also noted that the best discharge capacity is obtained for PbO$_2$ which contains 1% of graphene. It is at this percentage that we found a discharge capacity equal to 53mAh, while the discharge capacity obtained for PbO$_2$ alone is 40 mAh.

It can be said that the addition of 1-5% mass of graphene improves the electrical performance of the active material in a remarkable way. It seems that at the rate of a certain rate that we call a critical rate, the addition of graphene no longer has the desired effect. The addition of a large fraction of graphene negatively influences its electrochemical reactivity.It can be concluded that the increase in the utilization rate of the active ingredient was obtained for the low levels (1%) of graphene added. This increase can be attributed to an improvement in the electrical

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Table 2: Impedance electrical parameter values corresponding to PbO₂ and PbO₂-Gr powders (1%, 5%).

	PbO₂	PbO₂+1%Gr	PbO₂+5%Gr
R_1 (mΩ.cm²)	576.7	550.1	594.5
R_2 (Ω.cm²)	203.3	49.49	109.6
C_{dl} (mF.cm⁻²)	4.38	2.032	2.584
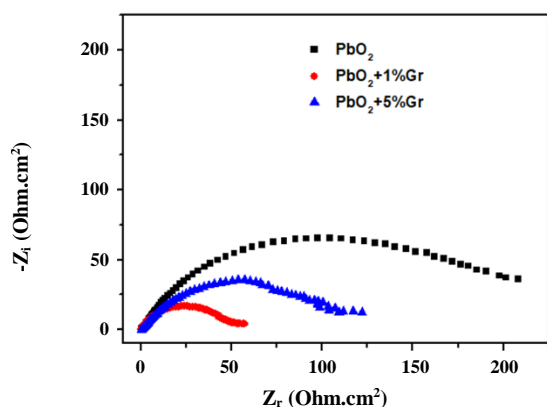
Fig. 6: Nyquist plots of PbO₂ and PbO₂-Gr powders (1%, 5%) in 1.28 M H₂SO₄ electrolyte.

conductivity of the active ingredient. In addition graphene has a high porosity. So it is able to absorb the electrolyte and thus favored its diffusion in the heart of the active material in discharge.

The impedance spectra of PbO₂ and PbO₂-Gr powders (1%, 5%) measured at open circuit potential (0.230 V vs.SCE) is shown as Nyquist diagrams in Fig. 6. The powders were analysed in 1.28 M H_2SO_4 electrolyte. All measurements were plotted on a frequency band ranging between 100 KHz and 100 mHz, with an alternative current voltage of 10 mV.

The Nyquist diagrams obtained in the form of a single capacitive loop, the semicircle diameter decreases with increasing graphene content in PbO₂ powder. Suggesting a decrease in resistance and the refore a significant increase in the electric conductivity of composite material containing graphene, this indicates that the graphenenanosheets can improve the interaction between conductive materials.

The Impedance electrical parameter values are showing in Table 2. Where R_1 is the electrolyte resistance, R_2 is the charge transfer resistance and C_{dl} is the double layer capacitance.

CONCLUSIONS

The study aims to investigate the influence of added graphene active mass of the positive lead-acid batteries electrodes in order to extend their lifework. We observed a remarkable improvement of the discharge capacity of the PbO₂ for an amount ofgraphene ranging between 1 and 5 %. In addition, the graphene with its high porosity facilitates the transport of the electrolyte throughout the positive active mass.

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