

## Electrochemical Investigation of Carbon as Additive to the Negative Electrode of Lead-Acid Battery

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**Abstract.** The increasing demand of cycle life performance of Pb-acid batteries requires the improvement of the negative Pb electrode's charge capacity. Electrochemical investigations were performed on Pb electrode and Pb+Carbon (Carbon black and Graphite) electrodes to evaluate the ability of the additives to enhance the electrochemical faradaic reactions that occur during the cycle of Pb-acid battery negative electrode. The electrodes were characterized through Cyclic Voltammetry (CV), Potentiodynamic Polarization (PP), and Electrochemical Impedance Spectroscopy (EIS). CV revealed that the addition of carbon on the Pb electrode increased anodic and cathodic reactions by tenfold. The kinetics of PbSO<sub>4</sub> passivation measured through PP revealed that the addition of Carbon on the Pb electrode accelerated the oxide formation by tenfold magnitude. The Nyquist plot measured through EIS suggest that the electrochemical mechanism and reaction kinetics is under charge-transfer. From the equivalent circuit and physical model, Pb+CB1 electrode has the lowest EIS parameters while Pb+G has the highest which is attributed to faster faradaic reaction. The Nyquist plot of the passivated Pb+CB1 electrode showed double semicircular shape. The first layer represents to the bulk passive PbSO<sub>4</sub> layer and the second layer represents the Carbon+PbSO<sub>4</sub> layer. The enhancements upon addition of carbon on the Pb electrode were attributed to the additive's electrical conductivity and total surface area. The electrochemical active sites for the PbSO<sub>4</sub> to nucleate and spread increases upon addition of electrical conductive and high surface area carbon additives.

### 1 Introduction

The increasing demand of cycle life performance of Lead-acid (Pb-acid) batteries requires the improvement of the negative lead electrode [1]. One application is for new generation transportation vehicles such as Hybrid Electric Vehicles (HEV), at which the Pb-acid battery requires continuous operation and being able to accept charge and discharge at extreme high rates [2, 3]. During the discharge of a Pb-acid battery, the negative electrode reacts with the sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) electrolyte to form non conducting lead sulfate (PbSO<sub>4</sub>) [4]. The buildup of PbSO<sub>4</sub> at the negative electrode during the repeated cycle of charge and discharge of the Pb-acid battery is deleterious to its operational life due to decreased electronic conductivity and reduced active sites. The negative electrode of Pb-acid battery were perceived as the life-limiting component as the accumulation of PbSO<sub>4</sub> becomes thicker with further cycling which leads to reduction of capacity and premature failure [4, 5].

The negative electrode performance is strongly influenced by its paste additives composed of lead oxide, sulfuric acid, water, and carbon/oxide additives. The chemical and physical properties of the active material which is dictated by the additives must be capable of meeting the charge and discharge capacity. The technical challenge to be met in maximizing the capacity involves

the improvement of charge acceptance and cycleability by increasing the conductivity and surface area of the negative electrode [5, 6].

Several studies have shown that the PbSO<sub>4</sub> buildup on negative electrode can be dramatically reduced by introduction of carbon on the negative active layer [7-10]. The influence of the carbon additives on the electrochemical performance of Pb-acid battery is governed by their material characteristics such as average particle size, total surface area and electrical conductivity. Reports of Pavlov [7, 8] shows that the addition of Carbon Black into the negative active layer have improvements on battery performance during the simulated electrical test. Reports of Baca [9] and Fernandez [10] reported that the addition of Graphite and Graphite-Carbon combinations into the negative electrode have significant beneficial effects on the capacity and cycle life of Pb-acid battery.

Selection of different additives on the negative electrode is time consuming and expensive exercise as it is usually evaluated at battery level which includes battery making and testing. Electrochemical techniques such as Cyclic Voltammetry (CV), Potentiodynamic Polarization (PP), and Electrochemical Impedance Spectroscopy (EIS) performed at electrochemical cell level can deliver faster and accurate information for the operation performance of the negative electrode.

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Electrochemical techniques will help for rapid evaluation and selection of different additives and can be the basis for defining reliable method of additive selection [11].

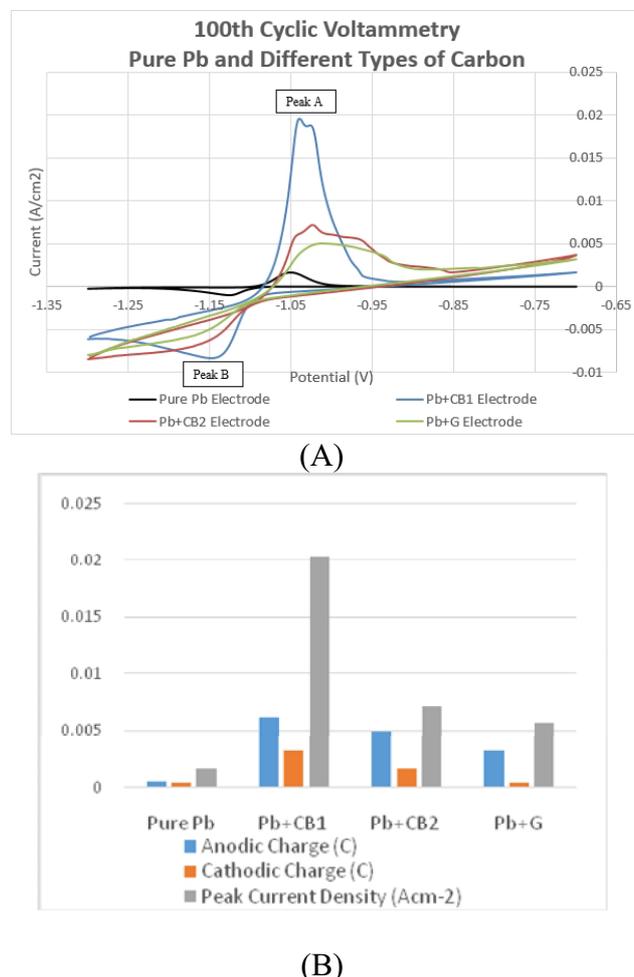
This research aims to determine the influence and mechanism of different carbon materials (Carbon black and Graphite) as additives on the negative electrode of Pb-acid battery to improve its charge acceptance and cycleability. The electrode was characterized through electrochemical cell using Cyclic Voltammetry, Potentiodynamic Polarization, and Electrochemical Impedance Spectroscopy. The data gathered from this research will contribute to the development of carbon and oxide as additives to the negative electrode of Pb-acid battery, and for the development of electrochemical techniques in the selection of appropriate additives to the negative electrode of Pb-acid battery.

## 2 Cyclic Voltammetry: The effect of different carbon additives on the Pb electrode.

The cyclic voltammograms of Pb and Pb+Carbon electrodes after 100 cycles are presented in Fig. 1A. The voltammograms for the Pb and Pb+Carbon electrodes reflect the electrochemical faradaic reactions of Pb oxidation and reduction of PbSO<sub>4</sub> into H<sub>2</sub>SO<sub>4</sub> solution. The first peak (Peak A) correspond to the anodic process or the oxidation of Pb to PbSO<sub>4</sub> which can be associated with the discharge process on negative electrode. The second peak (Peak B) correspond to the cathodic process or the electroreduction of PbSO<sub>4</sub> to Pb, which can be associated with the charge process. During the positive (anodic) potential scan, the current density increases due to the electrochemical reaction on the Pb electrode. PbSO<sub>4</sub> layer forms on the electrode surface and a peak current appears in the current curve. The PbSO<sub>4</sub> layer exerts a passivating effect in the electrode thus resulting to rapid decline of current density after the peak current. During the cathodic scan, the PbSO<sub>4</sub> layer is reduced to Pb, yielding a cathodic current. The cyclic voltammogram obtained on Pb+Carbon electrodes with different carbon additives are similar to those of a double layer capacitor. Electrical double layer capacitors are energy storage devices in which the charges are stored at the interface between the active surface and electrolyte. The electrolyte ions are electrostatically adsorbed on the surface of the carbon electrodes [11, 12] The addition of carbon to the Pb electrode resulted into pronounced anodic and cathodic curves which suggest that the quantity of electricity generated by Pb+Carbon electrodes is higher than the electricity generated by the Pb electrode alone. The carbon attached on the surface of Pb electrode served as current collector which increases the anodic and cathodic curves by the order of 3 to 10x magnitude depending on the type of carbon additive.

The peak current density and capacities of anodic charge and cathodic charge of Pb+Carbon electrodes with different different carbon additives is presented in Fig. 1B. Peak current density corresponds to the highest current on the cyclic voltammogram. Addition of carbon on the Pb electrode increased the peak current density of

the anodic reaction which correlated to increase of the electron transfer during the electrochemical faradaic reactions of Pb oxidation and reduction of PbSO<sub>4</sub> into H<sub>2</sub>SO<sub>4</sub> solution. Among all the carbon additives, the highest peak current density was obtained from the Pb+CB1 while the lowest is from the Pb+G.



**Figure 1.** (A) 100<sup>th</sup> cyclic voltammogram of Pb and Pb+Carbon electrodes. (B) Data deduced from the cyclic voltammogram.

The anodic and cathodic charge capacity of the additives were obtained by quantifying the anodic and cathodic total area of the 100th voltammetric cycle. The increase of the anodic charge was attributed to the capacity of the Pb metal surface to form the PbSO<sub>4</sub> passive layer. Anodic charge capacity corresponds to the anodic process and associated with the oxidation of Pb to PbSO<sub>4</sub>. Cathodic charge capacity corresponds to the cathodic process and associated with the reduction of PbSO<sub>4</sub> to Pb. Addition of carbon on the Pb electrode increased the anodic and cathodic charge capacity tenfold. The highest anodic and cathodic charge capacities were obtained on Pb+CB1 electrodes while Pb+G electrode has the lowest. The enhancement of the anodic and cathodic charge capacity may suggest that the oxidation and reduction of Pb to PbSO<sub>4</sub> proceeds on the Pb surface and also on the carbon layer which improves the capacity of charge and discharge of the Pb electrode [11, 12].

### 3 Potentiodynamic polarization: PbSO4 passivation rate of different carbon additives on the Pb electrode

The kinetics of PbSO4 passivation was evaluated through the potentiodynamic polarization measurements. The rate of PbSO4 passivation of the different electrodes was calculated using the Butler-Volmer equation and Tafel constants. The potentiodynamic polarization curves of Pb and Pb+Carbon electrodes are presented in Fig. 2 and the computed values were tabulated on Table 1. The addition of Carbon the Pb electrode shifted the Open Circuit Potential (OCP) into positive direction. OCP or sometimes called corrosion potential is the equilibrium potential of the metal when electrode is immersed on the electrolyte and not connected to any electrical system. Pb electrode has more negative OCP with average value of -1.055V. Addition of carbon additives on the electrode shifted the OCP into more positive value (from -0.267V to -0.151V) which may be attributed to the acceleration of the oxidation of Pb to PbSO4. Literature [13, 14] stated that the shifting of OCP into positive values favors the kinetics of the passive film growth or anodic reaction on metal active surfaces. The shifting of OCP values into positive direction is an indication of protective layer present on the metal active surface and indication of more stable metal surface. At higher OCP, the nucleation and growth process under charge transfer control favours the formation of more but smaller PbSO4 crystals [15]. Among all the Pb+Carbon electrodes, Pb+CB1 has the highest (most positive) OCP values and Pb+G has the lowest (more negative).

Pb+G	-0.267	0.014	2.749	1.16	46.08	19.52
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The results of potentiodynamic polarization showed that the Pb electrode has passivation rate of 0.82mm/yr and passivation current density of 13.79  $\mu\text{Acm}^{-2}$ . Same range of corrosion rate and corrosion density were reported by several authors on Pb electrode [16]. Addition of carbon into the Pb electrodes increased the rate of PbSO4 formation up to x10 magnitude. Pb+CB1 electrode has the highest value of passivation rate and passivation current density which suggest that the Pb+CB1 electrode has the greatest tendency to form PbSO4 passivation than the rest of the carbon electrodes. Several literatures showed that the fine Pb surface, having increased in active sites, favored the formation of the PbSO4 passive film than the coarse Pb surface [14-16]. Addition of carbon on the Pb active surface increased the active sites and current collection which favored the formation of PbSO4 passive film.

### 4 Electrochemical impedance spectroscopy: PbSO4 passivation rate of different carbon additives on the Pb electrode

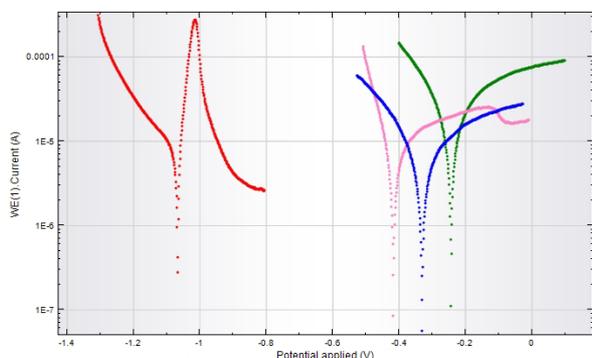


Figure 2. Linear polarization curves of the Pb+Carbon electrodes.

Table 1. Computed values from the potentiodynamic polarization curves.

Electrode	OCP (V)		Passivation Rate (mm/yr)		Passivation Density ( $\mu\text{A}/\text{cm}^2$ )	
	Mean	Sdev	Mean	Sdev	Mean	Sdev
Pure Pb	-1.055	0.001	0.82	0.125	13.79	2.1
Pb+CB1	-0.151	0.003	10.81	0.339	181.3	5.6
Pb+CB2	-0.188	0.006	4.91	0.63	82.47	10.7

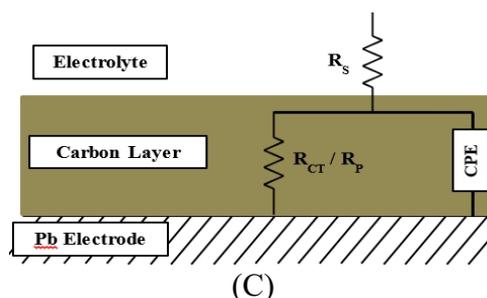
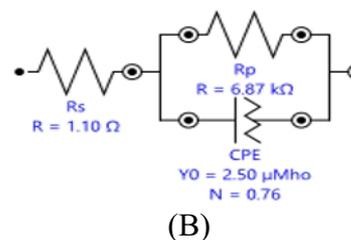
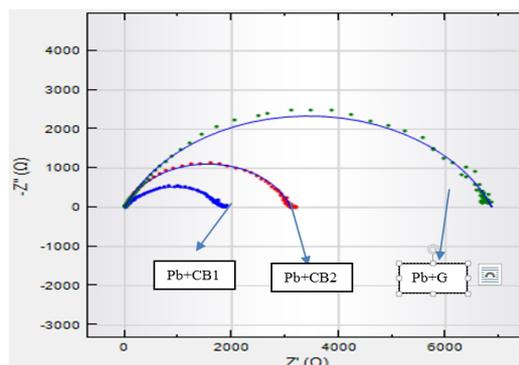


Figure 3. (A) Impedance spectra of the electrodes. (B) Equivalent circuit model. (C) Physical model of the electrode.

**Table 2.** Parameters deduced from the Impedance spectra.

Element	Pb+CB1 Electrode		Pb+CB2 Electrode		Pb+G Electrode	
	Value	% Error	Value	% Error	Value	% Error
$R_s$	1.05	3.993	2.4275	3.366	3.1031	3.202
$R_p / R_{CT}$	1846	0.132	3105.5	0.255	6867.5	0.544
CPE	1.17E-05	1.534	2.21E-06	1.28	2.50E-06	2.114
$\chi^2$	0.0502		0.023		0.093	

The Nyquist plot of the different Pb+Carbon electrodes is presented in Fig. 3A. The Nyquist plot for the Pb+Carbon electrodes have semicircular shape which suggest that the electrochemical mechanism and reaction kinetics is under charge-transfer or activation control which dictated by the rate of charge or electron flow [17-19]. The equivalent circuit model and the physical model of the electrode surface for different Pb+Carbon electrodes is presented in Fig. 3B and Fig. 3C, respectively. The elements in the model will be the basis of the various phenomena going on at the interface. Based from the Fig. 3C,  $R_p$  or  $R_{CT}$  is a measure of the charge transfer resistance of the carbon layer, CPE reflects the existence of capacitance or the charge stored in the carbon layer, and  $R_s$  is a measure of the electrolyte resistance or resistance of the layer to current flow. Table 2 summarizes the parameter values obtained from the Nyquist plot and equivalent circuit of Pb+Carbon electrodes. Among all the carbon additives, Pb+CB1 electrode has the lowest  $R_s$  and  $R_{CT}$  while Pb+G has the highest. Low  $R_s$  and  $R_{CT}$  mean fast faradaic reaction and the layer is conductive [17-19]. The CPE value for Pb+CB1 electrode is higher than the Pb+CB2 and Pb+G electrode which agree with the capacitor-like behavior of the Pb+Carbon voltammograph previously.

The enhancements upon addition of carbon additives on the Pb electrode were attributed with additive's electrical conductivity and total surface area. Carbon Black 1 having the highest electrical conductivity and finest particle size, resulted into more enhanced anodic and cathodic reactions by tenfold. The electrochemical active sites for the  $PbSO_4$  to nucleate and spread increases upon addition of electrical conductive and high surface area carbon additives.

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