Supplementary Information

Effect of graphene and carbon nanotubes in the negative active materials of lead acid batteries operating under high-rate partial-state-of-charge operation.

S. Mithin Kumar, S. Ambalavanan and Sundar Mayavan*

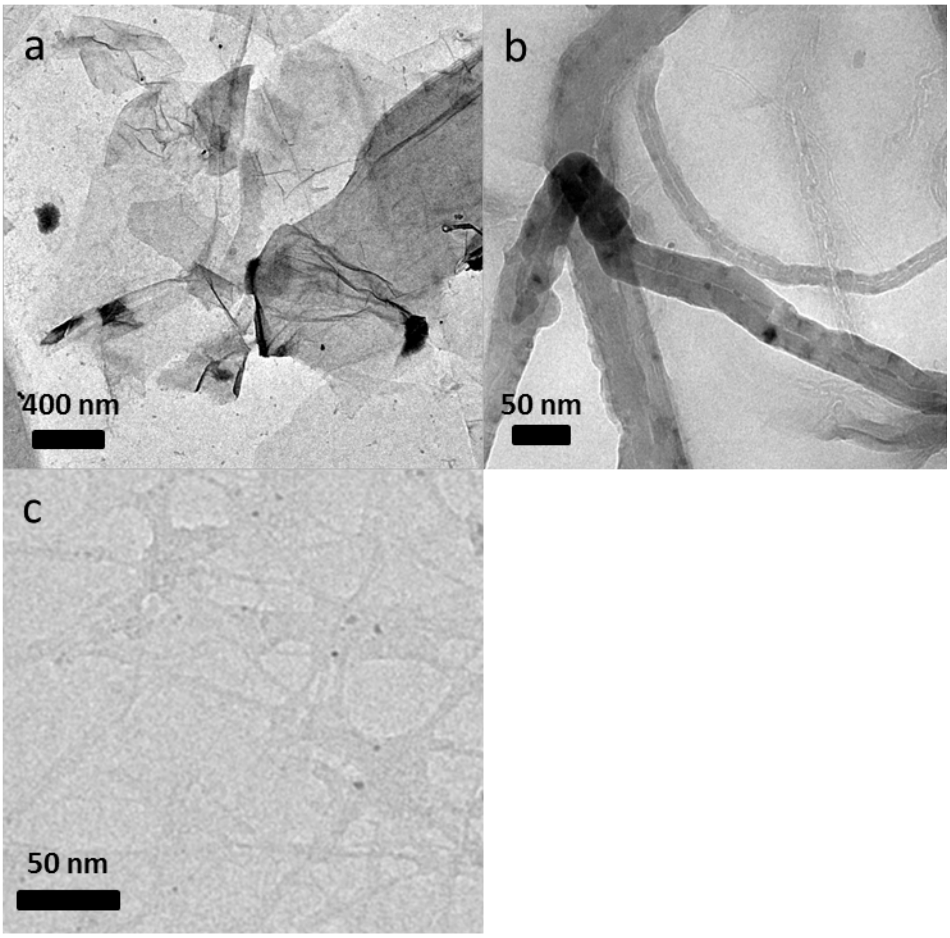

Figure S1: TEM images of pristine (a) graphene, (b) MWNT and (c) SWNT

Experimental

The effects of three nano-carbon materials were investigated: MWNT, SWNT and graphene powder. Table 1 summarizes the characteristics (as specified by the suppliers) of the three graphitic carbon materials used. The negative active mass were prepared using H_2SO_4, leady oxide and carbon additives. The carbon additive concentration is about 0.25 wt%.

Additive	Supplier	Ave. Length	Size	Purity	Surface area
SWNT	Nano shell, USA	3-8 µm	1-2 nm (diameter)	> 98%	350-450 m^2/g
MWNT	SRL, India	5-15 µm	40-50 nm (diameter)	> 99%	-
Graphene	Nano shell, USA	1-10 µm	0.5-0.6 nm (thickness)	> 99.9%	250 m^2/gm

Table 1. Characteristics (as specified by the supplier) of the nano-carbon materials used as additive to NAM in the present study.

Cell assembly: Lead acid test cells (2 V/1.22 Ah) were assembled comprising one negative and two positive plates using lead-selenium alloy. Dimensions of negative and positive plates were 40mm X 49 mm X 1.5 mm and 40 mm X 49 mm X 2.0 mm respectively. The negative lead paste was prepared by conventional method. In the conventional method, negative active material was prepared by mixing grey oxide (73% PbO + 27% free Pb), expanders ($BaSO_4$ 0.3 %), lignin (0.3 %) and nano-structured carbons (0.25%) in a sigma mixture. Dry mixing was carried out for 2-3 minutes. Then demineralized water was added as quickly as possible into dry mix. Then H_2SO_4 (sp.gr 1.25) was added as slowly as possible in order to prevent the paste temperature going above 60ºC. Finally small portion of water was added (during mixing) to bring the paste to proper consistency. The finished paste was applied to the grid. Then the plates are cured under carefully controlled conditions of time (48 hour), temperature (< 60 ºC) and humidity (> 90 ºC). Then dried plates are electrolytically oxidised and reduced in dilute H_2SO_4 (sp.gr 1.05) solution. Finally the cells were assembled with PVC separator. The cells were filled with 40 mL of 1.25 sp.gr sulphuric acid (H_2SO_4). The performance of the cells was limited by the negative plate. The charge-discharge tests were carried out using Bitrode life cycle tester.

Test program: Firstly, the assembled cells were subjected to 20 h and 10 h rate cycling (10 cycles) at room temperature. Secondly, the cell performance was evaluated under simulated HRPSoC conditions, using a simplified profile imitating micro-hybrid driving mode. Firstly, the assembled cells were subjected to 20 h rate cycling (10 cycles) at room temperature. Secondly, the cell performance was evaluated under simulated HRPSoC conditions, using a simplified profile imitating micro-hybrid driving mode.[11,12] The cells were subjected to cycling according to the following schedule. Charge at 2 C rate for 60 s, rest for 10 s, discharge at 2 C rate for 60 s, rest for 10 s. The test was stopped when the end voltage reaches 1.83 V or when the upper voltage limit of 2.83 V was reached. The above-described cycling steps comprise of one cycle-set of the test. After this cycle set, the cell was fully re-charged (to 100% SoC) and their C20 capacity was measured then followed to second cycle-set. The charge–discharge tests were carried out using Bitrode life cycle tester. Upon completion of the cycling test, negative active mass (NAM) was removed from the grid and analysed by X-ray diffraction (XRD) and Scanning Electron Microscopic (SEM). Scheme 1 presents a summary of the negative plates prepared with the three different types of nano-carbons and of the types of tests and analyses performed in this work.

Instrumentation: Raman spectra were recorded using a high resolution Renishaw Raman microscope employing a He-Ne laser of 1 mW at 514 nm. X-ray diffraction (XRD) patterns of the samples were measured using Bruker D8 Advance X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) measurement was performed with Sigma probe X-Ray Photoelectron Spectrometer (Thermo VG Scientific) with Al Kα X-ray for excitation. The Field-emission Scanning electron microscopy (FE-SEM) images are done with Carl Zeiss SEM instrument (model number: Supra 55VP/41/46) with an accelerating voltage between 15 kV using SE detector. Energy-dispersive X-ray (EDX) analysis was obtained with an EDX detector installed on the same FE-SEM. Porometric data for NAM was performed on Micrometrics mercury penetration porosimeter. BET surface area data for NAM was done on Autosorb- iQ gas absorption analyzer (Quantochrome, Nova Instruments). A Philips-Tecnai F20 field-emission transmission electron microscopy (FE-TEM) apparatus operated at 200 kV was used to observe the morphology of pristine graphene and carbon nanotubes. The samples for TEM were prepared by placing a drop of the aqueous dispersion of graphene and carbon nanotubes on carbon-coated copper grids followed by drying.

Carbon oxidation (by oxygen from positive plate).

In addition to oxidation of carbon (under open circuit potential of the LAB), carbon can also be oxidized by oxygen from positive plate.

In a lead acid battery: At the positive plate two major reactions takes place (grid corrosion and oxygen evolution)

Grid corrosion: $PbO_2 + Pb\ (grid) + 2H_2SO_4 \Leftrightarrow 2PbSO_4 + 2H_2O$ (1)
Oxygen evolution: $PbO_2 + H_2SO_4 \Leftrightarrow PbSO_4 + H_2O + 1/2O_2$ (2)

Basically the reaction (2) discharges the positive plate and forms oxygen gas. With the evolution of oxygen, the oxygen cycle starts, in which the oxygen (from the positive plate) oxidizes the negative plate consisting of lead and carbon additives.[1]
K. R. Bullock, *J Power Sources*, 2010, **195**, 4513.