

Effect of boron-carbon-nitride as negative additive for lead acid batteries operating under high-rate partial-state-of-charge operation.

S. Mithin kumar, Uday Venkat Kiran, Arockia Kumar Raju, S. Ambalavanan and Sundar Mayavan\*

### Supporting information

**Synthesis of BCN:** Calculated quantities of  $B_2O_3$ , Gly, and  $ZnNO_3$  were taken at a weight ratio of 1:2:2 ( $B_2O_3$ /Gly/ $ZnNO_3$ ) and sonicated (in water) to form a homogeneous solution. The homogeneous solution was thermally treated at 500 °C for 2 h at 2 °C  $min^{-1}$  under an argon atmosphere to form BCN sheets.

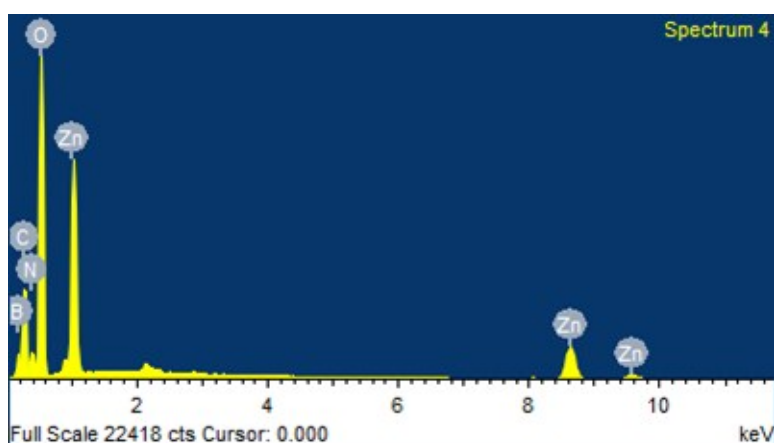


Figure S1: EDX spectra of BCN sheets

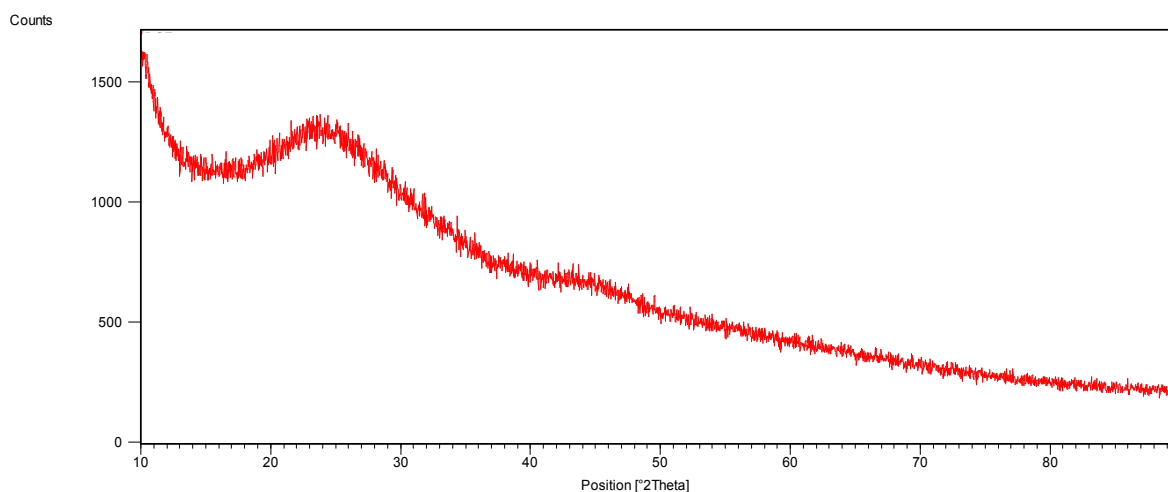


Figure S2: XRD diffraction pattern of BCN sheets

**NAM preparation and Cell assembly:** Two numbers of Lead acid test cells (2 V/ 3.2 Ah) were assembled comprising one negative and two positive plates using lead-selenium alloy in which one cell made with BCN as additive and another one is without BCN (i.e. using carbon black additive). 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 viz, BaSO<sub>4</sub> (0.3 %), lignin (0.3 %) and BCN (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<sub>2</sub>SO<sub>4</sub> (sp.gr 1.300) was added as slowly as possible in order to prevent the paste temperature going above 60°C. 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 °C) and humidity (> 90 °C). Then dried plates are electrolytically oxidised and reduced in dilute H<sub>2</sub>SO<sub>4</sub> (sp.gr 1.05) solution. Finally the cells were assembled with PVC separator. The cells were filled with 40 mL of 1.26 sp.gr sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). 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. 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).

**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 K $\alpha$  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 with and without BCN was performed on Micrometrics mercury penetration porosimeter. Cyclic voltammetric (CV) measurements were carried out on an electrochemical workstation (Solatron 1287 A) using a

conventional three-electrode cell with a platinum counter electrode and MSE (mercurous sulfate electrode) reference electrode.

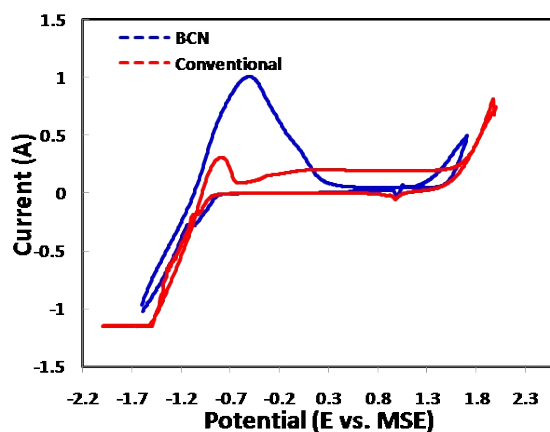


Figure S3: Cyclic voltammograms (vs. MMS electrode) of NAM with BCN and CB additive at scan rate 5 mV/s; electrolyte 1.28 g cm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>.

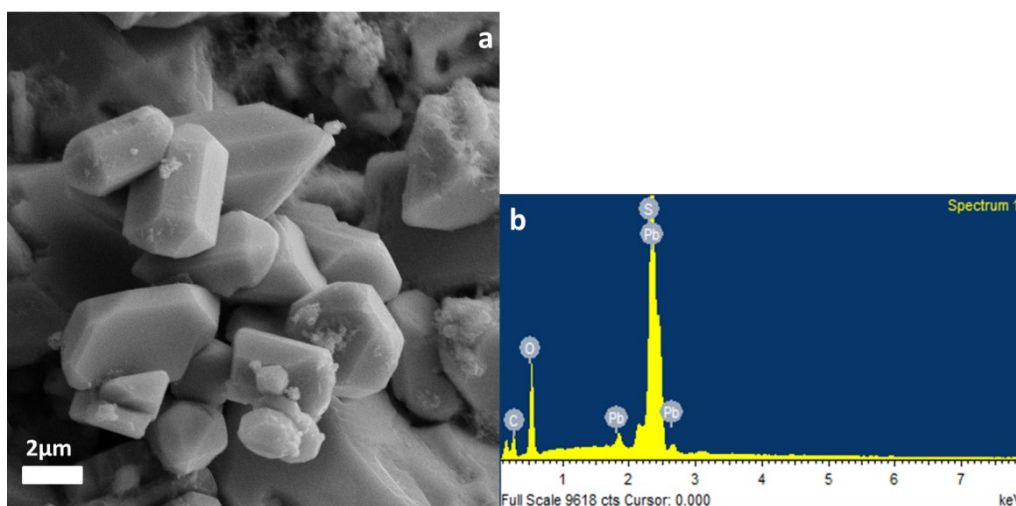


Figure S4: (a) FE-SEM image of failed NAM with CB added control cell showing the presence of PbSO<sub>4</sub> crystals after HRPSoC cycling; (b) EDX spectra showing the presence of Pb, S, O and C.

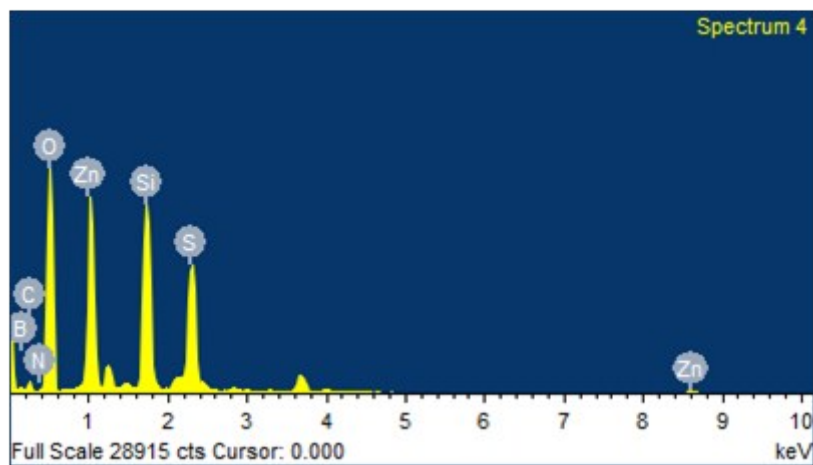


Figure S5. EDX spectra of as-prepared ZnO-BCN powder dissolved in  $1.28 \text{ g cm}^{-3} \text{ H}_2\text{SO}_4$  electrolyte showing the presence of B, C, N, Zn, S, O and Si elements (Si from glass plate onto which ZnO-BCN was coated)