Synthesis and application of carbon nitride enriched leady oxide as novel negative active mass for lead acid batteries

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ABSTRACT

In this work, we report the synthesis and utilization of carbon nitride enriched leady oxide (CNLO) as negative active mass (NAM) which enhances the charge–discharge characteristics of the lead-acid cells. The CNLO NAM were characterized by X-ray diffraction (XRD), Raman spectroscopy, Field emission scanning electron microscopy (FE-SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), respectively. Cells constructed with CNLO NAM exhibit remarkable improvement in the rate capability, active material utilization, cycle performance and charge acceptance compared to that of the cells constructed with conventional NAM.

1. Introduction

Lead acid battery invented in 1859 by Gaston Plante is the oldest rechargeable battery technology that is still being used widely for powering automobile, transportation and telecommunication industries [1–3]. In recent years, numerous attempts to improve the cycle life and capacity of the LAB have been made with the inclusion of carbon materials in negative active materials (NAM). Addition of carbon to NAM primarily improves its specific surface area [4,5]. Carbon in NAM reduces the sulfation of negative plates and extends the cycle life of cells [6–8]. Carbon in NAM improves the electronic conductivity by forming conductive networks between lead sulphate crystals [9,10]. Presence of carbon may impede the progressive growth of lead sulphate crystals [11–13]. The capacitive element of carbon can support charge and discharge events at high rates [4]. Addition of carbon not only changes the NAMs conductivity but also its microstructure and electrode reaction kinetics [14]. In all the reported approaches pristine leady oxide (LO) was used to form NAM. In this work, for the first time we report the successful synthesis and usage of carbon nitride enriched LO (CNLO) to form NAM. Lead acid cells constructed using CNLO NAM shows better performance and cycling properties as compared to conventional cells (with pristine LO NAM). The scheme towards preparation of CNLO is shown in Fig. 1.

2. Experimental

2.1. Synthesis of carbon nitride enriched LO (CNLO)

Calculated quantities of glycine and LO were dry mixed (10:1 wt ratio) and thermally treated at 250 °C for 2 h under air to form carbon nitride enriched LO (CNLO). CNLO is a mixture containing LO and carbon nitride in 10:0.3 wt ratio.

2.2. NAM preparation and cell assembly

Preparation of NAM: NAM was prepared by mixing CNLO or LO (78% PbO + 22% free Pb), $BaSO_4$ (0.3%), lignin (0.3%) and carbon black (0.25%). The above ingredients are dry mixed followed by the slow addition of calculated quantity of demineralised water and 1.300 specific gravity acid to form paste of proper consistency. The paste was then applied to grid and cured under controlled conditions. The cured plates were electrolytically oxidised and reduced in dilute sulphuric acid solution (sp.gr 1.05). PAM is also prepared following the same route but with only LO and Dynel fibres. 2 V/2.5 Ah lead acid cells comprising one negative and two positive plates were assembled using lead-calcium alloy (and a PVC separator). Dimensions of negative and positive plates were 68 mm × 39 mm × 1.5 mm and 68 mm × 39 mm × 2.5 mm respectively. Two cells one with CNLO NAM and other with LO NAM were assembled in this study. The performance parameters of the test cells were limited by the NAM.
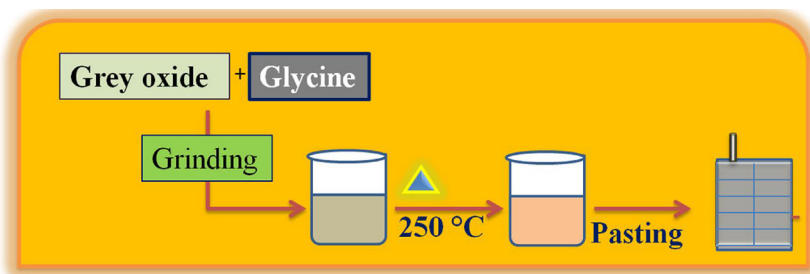
Fig. 1. Scheme towards preparation of CNLO.

2.3. Charge-Discharge cycling

Bitrode battery life cycle tester was used to perform the galvanostatic charge/discharge tests at various rates. In this study, experimental cells were initially subjected to 20 h (0.05C) rate of discharge for few cycles and further subjected to 10 h, 5 h, 2 h and 1 h rates. The subsequent overcharge for each rate of discharge was 110%. The cut off voltage varies with respect to rate of discharge and for high rate of discharge, voltage decreases from 1.75 V to 1.65 V.

2.4. 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. 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 5 kV using SE detector. BET experiment was carried out using NOVA Autosorb iQ surface area and pore size analysis. The pore size distribution plot was documented based on the Barrett Joyner- Halenda (BJH model). TEM images were recorded with Tecnai F20 using detector S-UTW with accelerating voltage between 20 and 200 kV. XPS analysis was carried out using thermo scientific ESCALAB 250XI with gun source Al K Alpha. Energy-dispersive X-ray (EDX) analysis was obtained with an EDX detector installed on the same FE-SEM. Cyclic voltammetric (CV) and Impedance measurements were carried out on an electrochemical workstation (IM 6 impedance analyser) using a conventional three- electrode cell with a platinum foil as counter electrode and MSE (mercurous sulphate electrode) as reference electrode. CV potential value is with respect to MSE.

3. Results and discussion

Polymeric graphitic carbon nitride (g-CN), a metal free semiconductor finds potential applications in various fields. They are structurally similar to graphite and shows high chemical and thermal stability. Thermal decomposition of amino acids results in the formation of ammonia, water and carbon di oxide. [15] In this work, carbon nitride was formed through decomposition of glycine at 250 °C (See Fig. 1 and experimental details). X-ray photoelectron spectrometer (XPS) was used to investigate the chemical bonding and configuration of carbon nitride formed by thermal decomposition of glycine. The survey scan (Fig. 2a) clearly shows the presence of nitrogen (N), carbon (C) and oxygen (O) with an atomic percentage of 25.45%, 63.05% and 11.49%, respectively. The high resolution N1s spectra (Fig. 2b) shows a major peak at 397.5 eV with a shoulder at 399. 1 eV. The peak at 397.5 eV relates to sp2 hybridized aromatic N bonded to carbon atoms. The peak at 399. 1 eV can be assigned to quaternary N bonded to three carbon atoms in the aromatic cycles [15]. The high resolution C 1s spectra (Fig. 2c) shows a major peak at 283.65 eV with shoulders at 285.05 and 287.05 eV which corresponds to graphitic carbon, C═N type carbon atoms and C─N type bonds, respectively.[16] The broad

XRD peak observed at 25.8° (002) for the as-prepared sample (Fig. 3a) indicated the formation of an amorphous CN structure [17]. The Raman spectrum (Fig. 3b) of the prepared sample, exhibits the D (at 1355 cm^{-1}) and G (at 1581 cm^{-1}) bands characteristic of amorphous carbon [16,18]. Raman results prove the formation of carbon nitride in the graphitic carbon nitride structures. Fig. 3c shows the TEM image of CN. TEM image reveal the presence of porous layered nanosheets. XPS, XRD, Raman and TEM data suggests conversion of Glycine to layered nitrogen rich CN sheets (on thermal treatment at 250 °C). Fig. 3d shows the XRD spectra of LO and CNLO (see Experimental and Fig. 1 for the synthesis of CNLO). XRD data suggests no significant difference between LO and CNLO except peak narrowing. Peak narrowing denotes reduction of lattice strain and increase in crystallinity. The average crystallite size (D) estimated from Scherer's equation was found to be 34 nm and 20.4 nm for CNLO and LO respectively. FE-SEM data (Fig. 3e and f) suggests agglomeration of LO particle upon thermal treatment. Fig. 3g, h shows the HRTEM image of the as-prepared CNLO. The HRTEM images shows the clear presence of highly aggregated oxide particles along with CN sheets. The surface area of the samples were analysed by BET, LO (23.45 m^2/g) shows slightly lower value as compared to CNLO (25.07 m^2/g).

The as-prepared CNLO was used to prepare NAM. Fig. 4a shows the XRD data of the formed NAM with LO and CNLO. Both the samples show characteristic Pb and PbSO$_4$ peaks, XRD data suggests no significant difference between NAM prepared with LO and CNLO. Fig. 4b shows the Raman spectroscopy of NAM formed with LO and CNLO. CNLO NAM show a broad weak bands around 1350 and 1580 cm^{-1} (highlighted in the Figure) which corresponds to the characteristics of (D) and (G) band along with characteristic lead peaks. But pristine NAM (with LO) shows clear lead peaks with complete absence of D and G bands. This is a clear indication for the presence of CN domains along with LO in CNLO NAM. Fig. 4c shows the CV curves of NAM with LO and CNLO. In the anodic sweep, the potential region, Pb is oxidised to PbSO$_4$. Meanwhile in the cathodic sweep, the formed PbSO$_4$ was reduced to spongy Pb. The inclusion of CN in the LO does not affect the electrochemical behaviour of NAM. No new reductive peaks or oxidative peaks are seen, and the peak potential does not shift significantly. Moreover, the peak current value of the NAM with LO and CNLO is comparable, which means that CN inclusion does not have any nonfaradic contribution (electric double layer). The current density is always a key factor to indicate the hydrogen evolution rate at over-charge condition [19]. The CNLO NAM shows high over potential for hydrogen evolution reaction and the hydrogen evolution current of CN LO NAM is only 45% of LO NAM. It states CNLO has great restraint action on hydrogen evolution and the hydrogen evolution performance (reducing the hydrogen evolution current by 45% and negatively shifting the onset potential), which means CN is an effective additive to depress hydrogen evolution. XPS data indicates clear presence of nitrogen groups in CN. Nitrogen being strongly electronegative can attract electrons from the neighbouring carbon atoms and make them electron deficient, and weakens the bond strength to hydrogen. Thus, hydrogen adsorption is hindered and hydrogen evolution is greatly inhibited in presence of CN domains.[19] But conventional LO (without nitrogen