Titanium dioxide-reduced graphene oxide hybrid as negative electrode additive for high performance lead-acid batteries

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A B S T R A C T

Sulfation at the negative electrode is one of the major failure modes of lead-acid batteries. To overcome the issues of sulfation, we herein report solvothermal synthesis of titanium dioxide- reduced graphene oxide hybrid as negative electrode additive in lead acid cell. The presence of titanium dioxide-reduced graphene oxide hybrid additive (0.5 wt. %) provides high interfacial stability, slows down hard sulfation, high active material utilization by occupying pores on the negative plate. 0.5 wt. % of titanium dioxide-reduced graphene oxide hybrid (3:1 wt. ratio) additive to the negative active mass delivers 85% increase in capacity during the first formation cycle, and thereby increases the formation efficiency from 3 cycles to 1 cycle; > 20% and ~200% increase in capacity at low discharge rates of C/20 and high rates of discharge (2C), respectively as compare to conventional lead acid cell. Besides, 3:1 wt. ratio titanium dioxide-reduced graphene oxide hybrid additive cells show ~200% increase in high rate partial state of charge cycle life in relation to conventional cell. Titanium dioxide-reduced graphene oxide hybrid additives to the negative active mass provides increase in conductivity, controls the crystallization of lead sulphate growth, acts as a capacitor, decreases the hydrogen evolution and hence enhances the electrochemical performance.

1. Introduction

Even though Lithium-ion batteries have growing interest in automotive and stationary energy storage, its 'predecessor' lead acid batteries (LAB) still plays a major role in automotive, solar, and telecommunication applications on cost grounds. There are several important challenges such as grid corrosion, sulfation at the negative plates are associated with lucrative growth and prospects of LABs in these applications. Grid corrosion and sulfation are the major cause why batteries prematurely fails [1]. At partial state of charge (PSoC) deep-cycle batteries used in off-grid in boats, cabins, rural telecom and inverter, backup systems are heavily cycled, and are often never fully recharged on a regular basis. Solar panels, which are not working properly in intermittent weather conditions or in shady areas often faces the PSoC related issues [2–5]. PSoC operations can quickly reduce the battery life because of thick sulfation, which results in frequent, costly battery replacements.

Valve-regulated lead-acid (VRLA) batteries used in hybrid electric vehicles (HEVs) operates at high rate partial state of charge (HRPSoC) within state-of-charge (SoC) window of 30–70%. In this condition, VRLA batteries cannot deliver cranking current when SoC is below 30%

or cannot accept charge from regenerative breaking or internal combustion engine when SoC is > 70%. LABs prematurely fails due to the accumulation of inherent PbSO$_4$ on the negative plate [6–10]. To overcome the issues of sulfation and poor charge acceptance, lots of research have been carried out to improve the conductivity of active material.

In the recent years, carbon based additives to the active mass have been proposed to address the issues of sulfation and charge acceptance [11–27]. To overcome different modes of operations like PSoC, HRPSoC, addition of different forms of carbon such as carbon black [11,12], graphite [13], activated carbon [14,15], carbon nanotubes (CNTs), single walled carbon nano tubes (SWCNTs), Multi walled carbon Nano tubes (MWCNTs) [16–19], 3D-RGO [20] have been used to extend cycle life due to reduced sulfation. Few percentage (0.1–2 wt. %) of carbon addition to negative active mass (NAM) is considered as best strategy to create additional new functionalities, as it tunes both the electrical and structural properties of the material.

Carbon additives to the NAM provides enhanced conductivity, controls the crystallization of PbSO$_4$ growth, acts as a capacitor, decreases the hydrogen evolution and provides the nucleation sites [21–23]. Because of high conductivity and high surface area, addition

of carbon to the negative active mass increases the contact between active mass and electrolyte, reduces the formation time [24–27]. Addition of 0.5 wt. % carbon black to the negative active material decreases the lead sulfate concentration in lead acid battery thereby enhancing PSoC cycle life in HEVs and Photovoltaic applications. 1.5 wt. % of graphite additive to the negative active material improve the charge acceptance and 20–25% increase in cycle life in relation to the carbon black additive [11–13]. It is reported that 2 wt. % of activated carbon added to the negative active material improve the cell performance due to the new porous skeleton formed with negative active material. Activated carbon acts as capacitor and electrolyte absorber in negative active material [14,15]. Incorporation of 0.008-0.02 wt.% of CNT to the negative active mass increases the conductivity and charge acceptance thereby increases cycle life from 170 cycle to 360 cycles in flooded SLI type batteries at 25% of depth-of-discharge [18]. Incorporation of 1% of 3D-RGO into the negative active material increases the HRPSoC cycle life by the 224% from 8142 to 26,425 cycles, due to the excellent porous structure and conductivity of the 3D-RGO [20]. In overall carbon-based additives improves the conductivity, charge acceptance, and facilitate the dissolution of big $PbSO_4$ crystals with less surface coverage, thereby enhances battery performance and cycle life.

Besides carbon additives, metal oxides such as Bi_2O_3, Ga_2O_3, and In_2O_3 etc. used as NAM additive to improve reversibility of the negative electrode. Addition of electrochemically active carbon (EAC) to negative active material mitigates the sulfation and required amount of In_2O_3, Ga_2O_3 and Bi_2O_3 in EAC decreases the hydrogen evolution rate, decreases the charge cutoff voltage and boost the discharge cutoff voltage [28,29]. Among metal oxides, the effect of TiO_2 is mostly studied due to its well- defined chemical composition, availability and efficiency. Addition of TiO_2 in the NAM provides steric hindrance to the crystals of $PbSO_4$ in the electrode pores. The active material resistance and hydrogen over potential were negligible for TiO_2 additive-based negative electrodes. It was found that addition of 2.5 wt. % of TiO_2 in the negative plates showed good cyclic stability of about 205,000 cycles under PSoC cycle tests. Higher concentration (5%) of TiO_2 in the NAM does not deliver good electrochemical performance due to blocking of pores completely with the excess of TiO_2 additives. While less concentration of 0.5 wt. % or 1 wt. % also does not show good performance as TiO_2 is not sufficient to occupy the larger pores. Due to which aggregation of lead sulfate crystal can occur during discharge and can lead to degradation of the battery cycling performance [30–32].

In this work, we have investigated titanium dioxide – reduced graphene oxide (TiO_2-RGO) hybrid as an additive to the NAM, which would overcome kinetic issues due to sulfation. The presence of TiO_2-RGO hybrid additive provides interfacial stability (improves the charge efficiency), slows down hard sulfation, high active material utilization by occupying pores of the negative plate. TiO_2 maintain the electrolyte at the interior of the plate while RGO maintains conductivity of the plate thereby reducing hard sulfation. TiO_2-RGO hybrid was not used as an additive to the positive active material (PAM) as oxygen evolution at the PAM of lead-acid battery during charge could oxidize to carbon-to-carbon dioxide. Formation of carbon dioxide can increase the internal pressure of the cell and could cause water loss and evolve gasses.

2. Experimental

2.1. Synthesis of TiO_2-RGO hybrid material

Graphene oxide (GO) was initially synthesized from graphite (China Steel Corporation, Taiwan) using a modified Hummer's method [33]. In brief, 0.5 g graphite powder and 0.5 g $NaNO_3$ (Sigma-Aldrich) were mixed with 23 ml of concentrated sulfuric acid (98%) in a round bottom flask followed by magnetic stirring in an ice bath for 4 h. 3 g $KMnO_4$ (Sigma-Aldrich) was added slowly into the suspension at $0 \pm 1\,^\circ C$ followed by rest at $35\,^\circ C$ for 1 h. 46 ml of deionized water was slowly

added and the suspension was heated up to $98\,^\circ C$ under reflux conditions, and maintained for 2 h. Then it was stirred for 1 h after adding 100 ml water followed by 5 ml of 30% of H_2O_2 added to end the reaction. Thereafter, the suspension was washed with deionized water and HCl solution until it attains a pH of 5. Finally, the solution was filtered and kept it in vacuum oven at $60\,^\circ C$ for overnight to obtain GO.

Further, solvothermal synthesis route was employed for the preparation of TiO_2-RGO hybrid using the synthesized GO and commercial grade TiO_2 (Sigma-Aldrich) [34]. For solvothermal synthesis, 15 mg of GO was mixed into a solution of 45 ml of deionized water and 15 ml ethanol under sonication for 1 h to re-exfoliate GO thoroughly. 1.5 g of TiO_2 powder added into the GO suspension. The mixture was sonicated for 2 h. and stirring for 30 min. Sonication and stirring was continued until a homogeneous suspension of a uniform light gray color achieved. The suspension was poured into a Teflon-lined autoclave and maintained at $120\,^\circ C$ for 3 h. Finally, the suspension filtered and dried in vacuum oven at $60\,^\circ C$ for overnight to obtain the TiO_2-RGO hybrid having a wt. ratio of 100:1. Similarly, the other samples of TiO_2-RGO hybrid having different compositions of 3:1 and 10:1 wt. ratios were also synthesized. A detailed stepwise illustration of the solvothermal synthesis of TiO_2-RGO hybrid shown in Supplementary Fig. S1.

2.2. Structural and physical characterizations

The structure and morphology of the GO, RGO, TiO_2 and TiO_2-RGO hybrid were characterized using X-ray diffraction studies (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The phase structure identification of samples was carried out using Panalytical X'pert pro diffractometer (reflection $\theta - \theta$ geometry, Cu Kα radiation, receiving slit of 0.2 mm scintillation counter, 40 mA, 40 kV). Raman spectra of RGO, TiO_2 and TiO_2-RGO hybrid obtained by using a micro-Raman spectrometer HR 800 (Jobin Yvon Horiba, France) with a He-Ne laser (excitation line 632.8 nm). Field Emission Scanning Electron Microscope (FESEM) images of the as prepared GO, RGO, TiO_2 and TiO_2-RGO hybrid (100:1, 10:1, 3:1 by wt.) were obtained using Carle Zeiss SUPRA™ 40 FESEM, Germany. Further, structural changes of the electrode material after cycling was characterized using XRD. For this purpose, NAMs were recovered from the lead-acid cells (LACs), washed with deionized water, dried at $60\,^\circ C$ for overnight and used for analysis.

2.3. Preparation of the plates and cell assembly

The TiO_2-RGO hybrid additive negative plate paste was prepared by mixing leady oxide (Pb_2O) (84.6 wt. %), lignin (0.2 wt. %), barium sulfate (0.15 wt. %), Dynel fibres (0.05 wt. %), TiO_2-RGO (0.5 wt. %) and aqueous H_2SO_4 of 1.4 specific gravity (7 wt. %) with de-ionized water (7.5 wt. %). Similarly, conventional negative plate was prepared by using leady oxide (85 wt. %), 0.1% of carbon black and other components such as lignin, barium sulfate, dynel fibers, aqueous H_2SO_4 and water in the above mixture was kept constant. The prepared negative active material paste was then pasted on the grids of 7 cm x 4.5 cm dimensions followed by curing at $65\,^\circ C$ with humidity of 95% for 24 h. Similarly, other modified negative plates were also prepared by using the additive (RGO, TiO_2, TiO_2_RGO hybrid (having different wt. ratios of 100:1, 10:1 and 3:1) incorporated in to the active material during paste preparation. The preparation of the positive plate paste discussed in our earlier publications [35–37] and used without any modification. Further, the lead acid cells were assembled with conventional (without additive) and modified TiO_2-RGO additive negative electrodes, and conventional positive electrodes. In order to see the effect of additives, the cells were fabricated using one negative and two positive plate's configuration (negative limited) with AGM separator and H_2SO_4 electrolyte having specific gravity of 1.25. The schematic of the steps involved in the preparation of negative plate paste followed by the fabrication of a 2 V/2.1 Ah LAC are shown Supplementary Fig. S2.