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High Specific-Energy Lead-Acid Batteries Through Organic Metals

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A novel room-temperature route to corrosion protect lead-coated plastic grids with an organic metal, namely, polyaniline, for producing commercial-grade high specific-energy 12 V/45 Ah lead-acid batteries is reported. The specific energy of these lead-acid batteries is found to be *ca.* 45 Wh/kg as against about 30 Wh/kg for conventional lead-acid batteries. It is believed that the study reported here will open up a new realm of possibilities for lead-acid battery development, and will contribute directly towards lowering the cost of both battery materials and manufacturing.

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The lead-acid battery is ubiquitous in the global rechargeable battery market, and in terms of value its present world sales are about US$ 20 billion per annum.[1] Although lead-acid batteries are considered a mature technology, significant research and development efforts are currently underway to enhance their specific energy,[2-14] which currently remains restricted to only about 30 Wh/kg owing to the high mass-density of lead.

In brief, Hammar *et al.*[3] reported a lead-acid battery in which the grids comprise a substrate made of a polymer, such as polyvinyl chloride, laminated with a thin lead/lead alloy foil. This approach reduces the weight of the battery grid, contributing to an increase in the specific energy of the battery. However, Hammar *et al.* did not appear to apply a corrosion resistant coating on the substrate. As a result, the grids become susceptible to corrosion in acid medium, thereby limiting the durability of the lead-acid batteries. Pinsky *et al.*[4] reported a positive grid coated with electrically conductive doped tin oxide for lead-acid batteries. Rowlette[5] has reported battery grids made of metallic substrates like aluminum or titanium or their alloys coated with lead/lead alloy. These metallic substrates still have unacceptably high mass-density. Accordingly, it is desirable to produce grids using substrates made of materials having a further lower mass density.

Tsuchida *et al.*[6] employed polyamide and glass fibers to construct the lead-acid battery grids. The weight of the grid is reduced, in comparison with conventional grid made entirely of lead/lead alloys, by using low-density polyamide to form a support structure, and a glass fiber sheet coated by a thin layer of lead/lead alloy to form the electricity-collecting part of the battery grid. However, a corrosion-resistant coating appears to be absent even on these grids, which makes the grids prone to acid corrosion. Timmons *et al.*[7] describe another approach to reduce the weight of lead-acid batteries with its plate made of nonlead substrates such as aluminum encapsulated by thin sheets of conductive foils of lead/lead alloy. However, this approach also suffers from inadequacies similar to those described earlier.

In another approach, Kurisawa *et al.*[8] have attempted to use the radio-frequency sputtering technique to form protective tin oxide coating on lead grids. But sputtering is generally a slow process, and since it happens to be a line-of-sight process, both sides of the grids cannot be coated simultaneously, unless a complex and expensive sputtering apparatus is employed. Accordingly, the cost of forming a corrosion-resistant coating on the grids by a sputtering process is likely to be high. Recently, Shivashankar *et al.*[15,16] have employed a cost-effective, thermally activated chemical reaction process to produce tin-oxide-coated plastic grids for lead-acid batteries. Ironically, however, positive plates constituting tin oxide-coated grids have been found to be unstable in lead-acid batteries at 0.5 V *vs.* $Pb/PbSO_4$ electrode. In the light of the aforesaid description, it is desirous to find a process, which allows a corrosion-resistant coating on lead-coated battery grids constituted from a lightweight and inexpensive material, usually having a low-melting point.

In this communication, we report a novel room-temperature process to corrosion protect lightweight lead-coated acrylonitrile butadiene styrene (ABS) grids by electroplating with polyaniline (PANI). The process is simple, and initial studies suggest that it can be extended to other organic metals such as polythiophene, polyparaphenylene, polypyrrole, etc., by chemically modifying their structures.

Experimental

Battery grids of dimensions 15.3 × 11.7 × 0.2 cm were injection moulded from AP78EP grade acrylonitrile butadiene styrene (ABS) plastic. The grids were then coated with a layer of copper. This was followed by a lead metal coating. The grids were subsequently corrosion protected with a PANI layer, as described below.

The lead-coated grids were placed in a bath containing 1 vol % aqueous solution of aniline in 0.3 N oxalic acid with each of the grids held between two symmetrically placed dimensionally stable platinum-coated titanium electrodes. A thin layer of PANI was subsequently electrodeposited on to the battery grids by applying a potential of 1.4 V across the grids and the counter electrodes.[17] The grids were finally washed with a copious amount of deionized water and dried in a hot air oven at about 65°C. The deposition of PANI on the grids was confirmed by cyclic voltammetry. The grids were carefully cut using a diamondwheel and a cross-sectional view of the various layers was obtained by a JEOL JSM 840A scanning electron microscope.

12 V/45 Ah AGM-VRLA batteries were assembled by series-stacking three positive and four negative plates in each cell, and group burning to make intercell connections. The positive and negative plates in the cells were separated by 2 mm thick AGM separator obtained from Nippon Sheet Glass Co., Japan. The cells were filled with the required amount of 4.5 M aqueous sulfuric acid and were kept for about 2 h to facilitate electrolyte soaking. The batteries were made positive-limited to facilitate oxygen recombination at the negative plates.

The batteries were formed over three cycles by charging them galvanostatically at C/10 rate followed by discharge at C/5 rate on a Bitrode LCN-power module interfaced to a data acquisition system. The batteries were subjected to various charge/discharge studies at varying rates at temperatures ranging between −20°C to 50°C in a temperature-controlled chamber.

Grid corrosion was studied by cyclic voltammetry in the potential range between 0.6 to 1.56 V *vs.* MMS reference electrode at a scan rate of 20 mV/s using an Autolab (PGSTAT-30). Industrial

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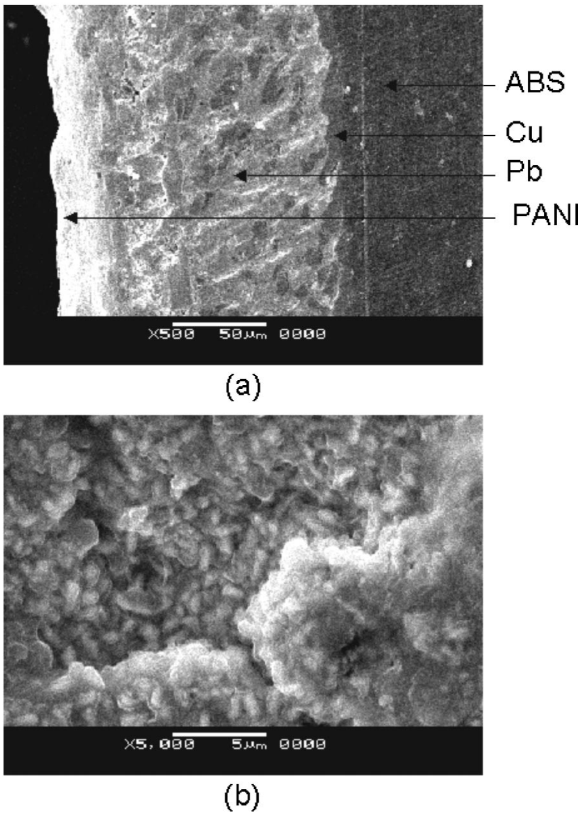

Figure 1. Electron micrographs depicting (a) cross-sectional and (b) surface morphology of ABS/Cu/Pb/PANI grids.

grid-corrosion experiments on the battery grids were also performed in a cell comprising a positive grid placed between two negative plates immersed in H_2SO_4 electrolyte maintained at 55°C. The grids were held potentiostatically at 2.5 V for 7 days and the variations in the current were recorded continuously. Subsequently, the grids were removed and washed thoroughly with deionized water. The corrosion layer on the positive grids was stripped by dipping them in an aqueous red-lead extraction solution comprising sodium acetate trihydrate, potassium iodide, and glacial acetic acid. The grids were finally washed thoroughly with deionized water and dried in a hot air oven at about 60°C. The corrosion rate was determined from weight loss measurements.

Cycle-life data on 12 V/45 Ah monobloc batteries were also obtained at 25°C employing a Bitrode LCN power module interfaced with a data acquisition system.

Results and Discussion

In order to determine the thickness of the various constituent layers in the coated grid, a cross-sectional scanning electron micrograph of the grid was obtained as shown in Fig. 1a. The micrograph shows an ABS base grid coated sequentially with a 10 μm thick copper layer, a 100 μm thick lead layer and a 1 μm thick layer of PANI. The PANI film comprises PANI particles of 0.1-0.2 μm as can be seen from the micrograph shown in Fig. 1b. The pattern of film growth, as depicted in Fig. 2a, suggests that growth in oxalic acid is entirely different from that in sulfuric acid, particularly due to the reducing nature of the former. Nevertheless, the PANI film obtained in oxalic acid gives a cyclic voltammogram characteristically similar to that in sulfuric acid (Fig. 2b). In order to examine the corrosion behavior of ABS/Cu/Pb (bare) and ABS/Cu/Pb/PANI (protected) grids in sulfuric acid, cyclic voltammograms for both the grid types were obtained in the potential range between 0.6 and 1.56 V *vs.* mercury-mercurous sulfate (MMS) reference electrode

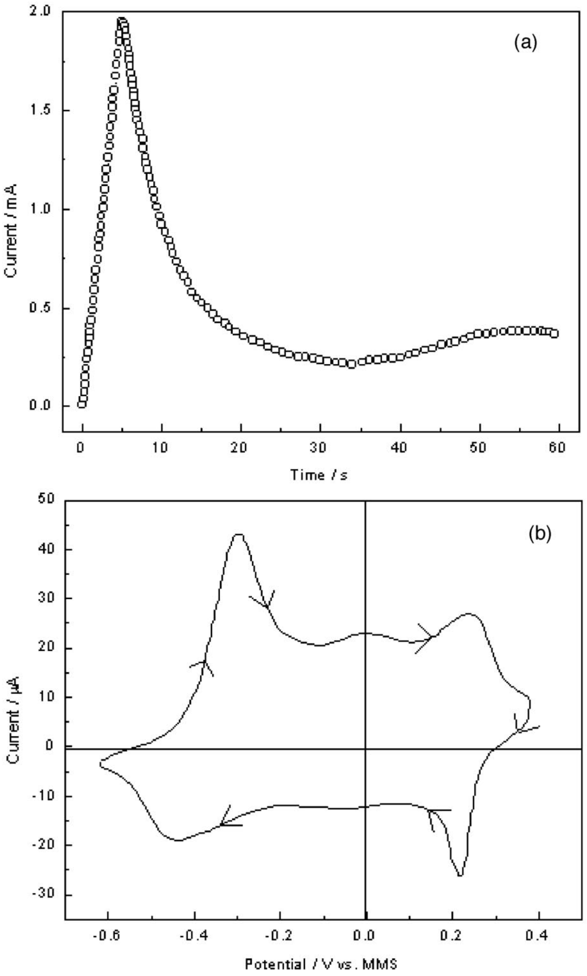

Figure 2. (a) Current *vs.* time response during PANI film formation at 1.4 V on a 0.25 cm^2 lead sheet in the presence of oxalic acid by potential-step technique, and (b) cyclic voltammogram of PANI deposited on a 0.25 cm^2 lead sheet in 1 M H_2SO_4 at a scan rate of 50 mV/s.

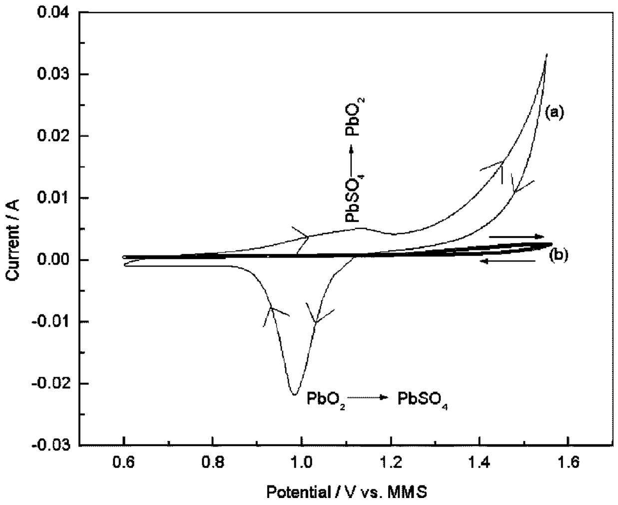

Figure 3. Cyclic voltammograms for (a) ABS/Cu/Pb (bare) and (b) ABS/Cu/Pb/PANI (protected) grids.

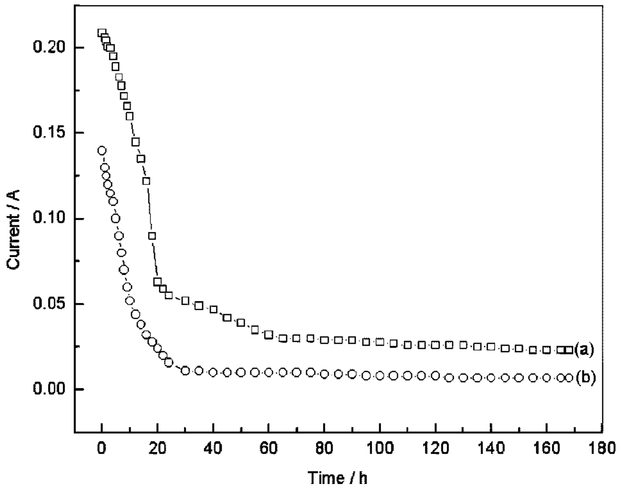

Figure 4. Comparative potentiostatic corrosion data for (a) ABS/Cu/Pb, and (b) ABS/Cu/Pb/PANI positive grids at a charging voltage of 2.5 V at 55°C.

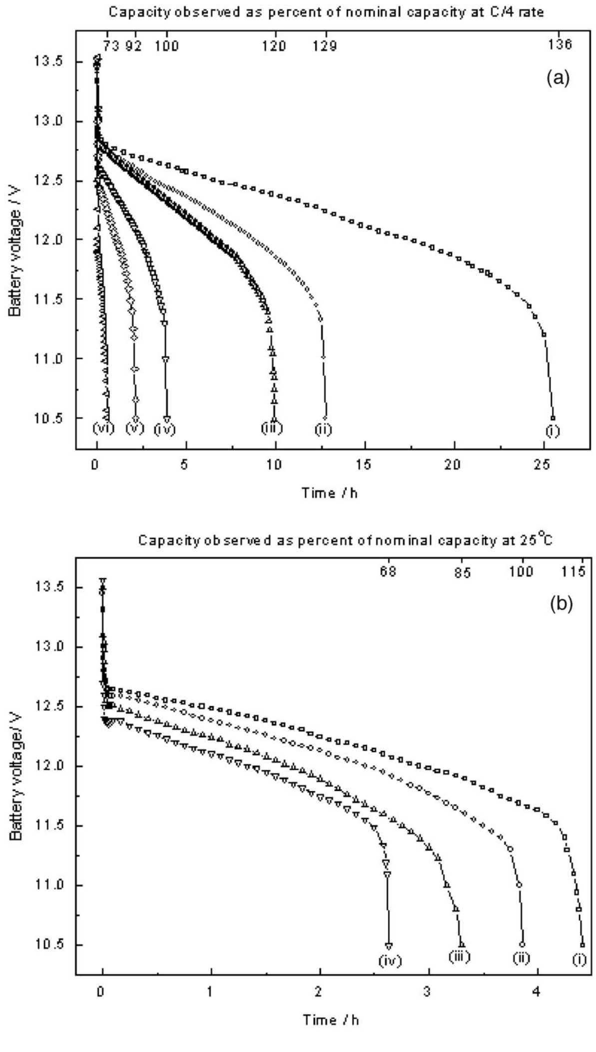

Figure 5. (a) Performance characteristics of a 12 V/45 Ah AGM-VRLA lead-acid battery with light-weight protected grids obtained at 25°C and (i) C/25, (ii) C/13, (iii) C/10, (iv) C/4, (v) C/2, and (vi) 2C discharge rates, and (b) effect of temperature on the discharge capacities of a 12 V/45 Ah AGM-VRLA lead-acid battery with light-weight protected grids obtained at C/4 rate at (i) 50, (ii) 25, (iii) 0, and (iv) −20°C.

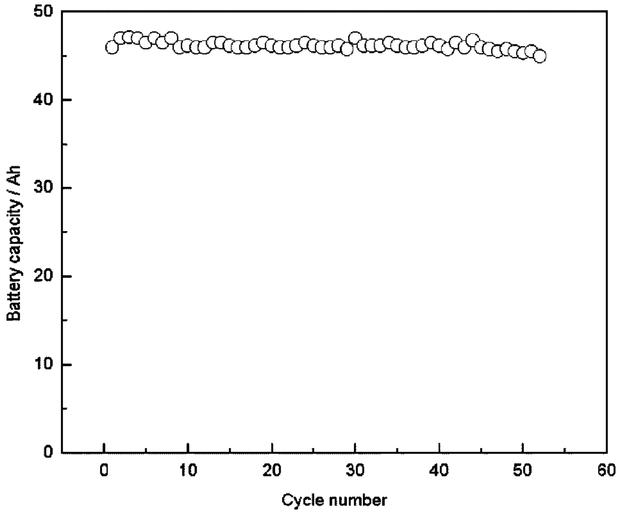

Figure 6. Cycle-life data for a 12 V/45 Ah monobloc battery with light-weight modified grids obtained at the C/4 rate at 25°C.

(Fig. 3). Interestingly, while the cyclic voltammogram of the ABS/Cu/Pb grid shows distinct peak currents at 1.10 and 0.95 V *vs.* MMS electrode, corresponding, respectively, to the oxidation of $PbSO_4$ to PbO_2 and reduction of PbO_2 to $PbSO_4$, a complete suppression of these peaks is noticed in the cyclic voltammogram for ABS/Cu/Pb/PANI grids, which suggests a significant mitigation of lead corrosion in the latter. Potentiostatic corrosion data obtained on ABS/Cu/Pb and ABS/Cu/Pb/PANI grids are shown in Fig. 4. The corrosion rates obtained from this study for the ABS/Cu/Pb and ABS/Cu/Pb/PANI grids were 2×10^{-3} and 2.2×10^{-4} g/cm^2/day, respectively.

After ascertaining the stability of the ABS/Cu/Pb/PANI grids in aqueous sulfuric acid (relative density = 1.25), the grids were pasted with appropriate active materials, assembled into 12 V/45 Ah AGM-VRLA batteries, and subjected to formation cycling. Typical galvanostatic charge-discharge data for the battery obtained at 25°C indicate a faradaic efficiency of about 90%. Performance characteristics of the battery at different rates ranging between C/25 and 2C, depicted in Fig. 5a, show that the battery exhibits a capacity increase of about 35% as compared to its capacity at the C/4 rate, while a proportionate decrease in capacity was observed at higher discharge rates of C/2 and 2C. Discharge data obtained at temperatures between 50 and −20°C, presented in Fig. 5b, indicate a 15% increase in battery capacity at 50°C in relation to that at 25°C; as expected, the capacity of the battery decreased at temperatures below 25°C. At an operating temperature of 25°C and at C/4 rate, the battery has sustained 50 charge-discharge cycles with little decay in capacity as shown in Fig. 6. There is no reason to believe that the battery engineering is yet fully optimized, and further improvements are highly likely.

Conclusions

The study provides a novel route to corrosion protect lead-coated lightweight plastic grids by electrodepositing polyaniline. Lead-acid batteries assembled with these grids have a specific energy value close to 45 Wh/kg. Such lead-acid batteries would be advantageous in conventional automobiles with internal combustion engines, as well as in hybrid electric vehicles, where fuel efficiency would be advanced when batteries are lighter.

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