A Low-Cost, High Energy-Density Lead/Acid Battery

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Lightweight plastic grids for lead/acid battery plates have been prepared from acrylonitrile butadiene styrene copolymer. The grids have been coated with a conductive and corrosion-resistant tin oxide layer by a novel rapid thermally activated chemical reaction process. X-ray powder diffraction and X-ray photoelectron spectroscopy show the coated tin oxide film to be SnO_2-like. The grids are about 75% lighter than conventional lead/acid battery grids. A 6 V/1 Ah lead/acid battery has been assembled and characterized employing positive and negative plates made from these grids. The energy density of such a lead/acid battery is believed to be more than 50 Wh/kg.

Currently available hybrid electric vehicles (HEVs) employ nickel-metal hydride (Ni/MH) batteries with energy densities of *ca.* 60 Wh/kg.[1] But Ni/MH batteries are expensive. HEVs could be made cheaper if cost-effective lead/acid batteries with energy densities similar to Ni/MH batteries could be developed. Nevertheless, due to the high mass-density of lead, the energy density of lead/acid batteries remains restricted to only about 30 Wh/kg.[2]

In the literature are reports[3-15] of several efforts expended to enhance the energy density of lead/acid batteries primarily by employing lightweight grid materials. Hammar and Harvey[3] reported a lead/acid battery in which the grids comprise a substrate made of a polymer, such as polyvinylchloride, laminated with a thin lead/lead alloy foil. This combination reduces the weight of the battery grid, contributing to an increase in the energy density of the battery. However, these authors do not appear to apply a corrosion resistant coating on the substrate. As a result, these grids become susceptible to corrosion in acid medium, thereby limiting the durability of the lead/acid batteries. Pinsky and Alkaitis[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 may still have unacceptably high mass-density; for example, aluminum has a mass density of 2.7 g cm^{-3}. Accordingly, it may be desirable to produce grids using substrates made of materials having a still lower mass density. Tsuchida and Imai[6] employed polyamide and glass fibers to construct a lead/acid battery grid. The weight of the grid is reduced, in comparison with conventional grids 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 reducing 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 addition to providing high energy density, it is desirable to produce cost-effective lead/acid batteries, which may be achievable only through the use of plastic-based substrate material. However, one problem with the use of such low-cost substrate materials is that these have low melting points, which makes them incompatible with several processes employed presently in the manufacture of lead/acid batteries. Similar incompatibility may also exist when applying an electrically conducting, corrosion-resistant coating on a lead/lead

alloy layer. For instance, the formation of such a corrosion-resistant coating as that of tin oxide on the lead/lead alloy layer of the battery grids usually requires a temperature appreciably higher than 327°C, the melting point of lead. In particular, the formation of a tin oxide layer by the simple and convenient dip coating method requires calcinations at a temperature in the range 450-600°C. Accordingly, Kurisawa *et al.*[8] have suggested that it is impossible to apply the dip coating method to a lead substrate, appearing to imply that the calcination temperature required to form the protective tin oxide layer by this method is incompatible with the lead/lead alloy grids.

Kurisawa *et al.*[9] have therefore attempted to use coating technologies that employ low substrate temperatures, such as vacuum-based thin-film technology, to form protective SnO_2 coatings on lead grids. Kurisawa *et al.*[9] report using the radio-frequency (rf) sputtering technique to deposit a 15 μm thick SnO_2 coating on a 500 μm thick lead plate. But sputtering is generally a slow process, which may require that the substrate, along with the lead/lead alloy coating, be subjected to ambient temperatures (~120°C) for many hours, potentially compromising the mechanical integrity of the grids. Furthermore, as sputtering is generally a line-of-sight deposition process, both sides of the grids cannot be coated simultaneously in a single step, unless complex and expensive sputtering apparatus is employed. Accordingly, the cost of forming a corrosion-resistant coating on a battery grid by such a sputtering process is likely to be high, which may not be suitable to battery production. Other efforts to develop high energy density lead/acid battery are directed toward more advanced research designs.[10-15]

From the foregoing, it is evident that to realize low-cost, high energy-density lead/acid batteries, it is desirable to develop a process, which allows the corrosion-resistant oxide coating on lead/lead alloy layer to be formed on battery grids constructed from a lightweight and inexpensive material, usually having a low melting point. Such grids may then be used to fabricate lead/acid batteries, which would have higher energy densities and a longer lifetime than conventional lead/acid batteries. In a recent publication, Bullock[16] has clearly documented that lead/acid battery research and development is vital to winning new business.

In this communication, we report a novel cost-effective, rapid thermally activated chemical reaction process (RTACRP) to produce tin oxide-coated plastic grids for lead/acid battery plates.[17] The process leads to a reduction of about 75% in grid weight as compared to conventional lead/acid battery grids. Accordingly, it is possible to realize lead/acid batteries with energy densities higher than 50 Wh/kg. This study thus opens up a whole realm of possibilities in lead/acid battery development, and promises to contribute directly toward lowering the cost of both materials and manufacturing.

Experimental

Plastic grids (dimensions: 45 × 20 × 2 mm) were molded from acrylonitrile butadiene styrene (ABS) copolymer. The grids were

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degreased ultrasonically in ethanol. These grids were then coated with a 10 μm thick copper layer by electroless deposition followed by a 100 μm thick lead layer deposited electrochemically. Subsequently, a 10 μm thick tin oxide coating was applied on the grids in a homemade rapidly heated furnace employing halogen lamps as the heating source. For this purpose, a viscous solution of stannous chloride ($SnCl_2$) was obtained by dissolving it in methanol. ABS/Cu/Pb grids were dipped in this solution and air-dried, and a coating of SnO_2 on the grids was applied by RTACRP. The formation of tin oxide takes ~5 s. The RTACRP equipment is simple and inexpensive, partly because it requires no vacuum pumps and related accessories.

Powder X-ray diffraction (XRD) patterns for the tin oxide-coated grids were recorded on a Siemens D-5005 X-ray diffractometer using Cu Kα radiation and were indexed using the PROSZKI algorithm.[18] X-ray photoelectron spectra (XPS) of commercially available SnO_2 powder sample and tin oxide films prepared by RTACRP were also obtained on an ESCA-3 Mark II VG-Scientific spectrometer with Al Kα radiation. The grids were carefully cut using a diamond-wheel to obtain the cross-sectional view of various layers deposited on the ABS grid using a JEOL JSM 840A scanning electron microscope (SEM).

Electrochemical characteristics of tin oxide coated grids were studied by cyclic voltammetry in the sweep range between 1 and 2.7 V *vs.* Pb/PbSO$_4$ electrode using an Autolab PGSTAT30 (EcoChemie, Utrecht, The Netherlands), with a BSTR10A current booster module. Grid-corrosion experiments on ABS/Cu/Pb/SnO$_2$ and Pb-Ca-Sn-Al alloy positive grids were performed keeping a negative plate on either side of the positive grid in a cell at 55°C, using 1.28 specific gravity aq H_2SO_4 as the electrolyte. For this purpose, the cell was charged potentiostatically at 2.5 V for 200 h and the variations in the current were recorded continuously. Subsequently, the grids were removed and washed with deionized (DI) water. The corrosion layer on the positive grid was stripped by dipping it in the red-lead extraction solution comprising sodium acetate trihydrate, potassium iodide and glacial acetic acid. The grids were finally washed copiously with DI water and dried in a hot-air oven. The corrosion rates were determined from the weight loss of the grids.

Both positive and negative plates of the lead/acid battery were prepared using ABS/Cu/Pb/SnO$_2$ grids to construct a 6 V/1 Ah battery in a Plexiglas container using 1.28 specific gravity aq H_2SO_4 as electrolyte, following an established industrial protocol. In brief, positive plate paste was prepared by mixing PbO (85 wt %), sodium carboxy methylcellulose (0.15 wt %), Dynel fiber (0.05 wt %), and aq H_2SO_4 of 1.4 specific gravity (7 wt %) with DI water (7.8 wt %). The negative plate paste was prepared by mixing PbO (85 wt %), lignin (0.2 wt %), barium sulfate (0.15 wt %), Dynel fiber (0.05 wt %), carbon black (0.1 wt %), and aq H_2SO_4 of 1.4 specific gravity (7 wt %) with DI water (7.5 wt %). The paste densities for positive and negative plates were 4.2 and 4.4 g cm^{-3}, respectively. After pasting the active materials onto the grids, the plates were subjected to hydrothermal curing. Three positive-limited lead/acid cells were assembled to construct the 6 V/1 Ah lead/acid battery by group burning of electrodes and intercell connectors. Galvanostatic charge-discharge tests at different rates between C/10 and 3C, and at temperatures ranging between 50 and −30°C, were conducted on such a lead/acid battery. The battery was also subjected to life-cycle test at C/5 rate at 25°C.

Results and Discussion

The powder XRD pattern of the as-prepared SnO_2 film is shown in Fig. 1. The XRD pattern agrees well with that of cubic SnO_2. The XRD pattern was devoid of any reflection due to $SnCl_2$ or any oxide of tin other than SnO_2.

To corroborate our XRD data, we obtained XPS of the SnO_2 film shown in Fig. 2. Binding energies reported here are with respect to C (1s) peak at 285 eV and are accurate to within ±0.2 eV. The O (1s) peak in the SnO$_x$ film is observed at 531 eV, which agrees well
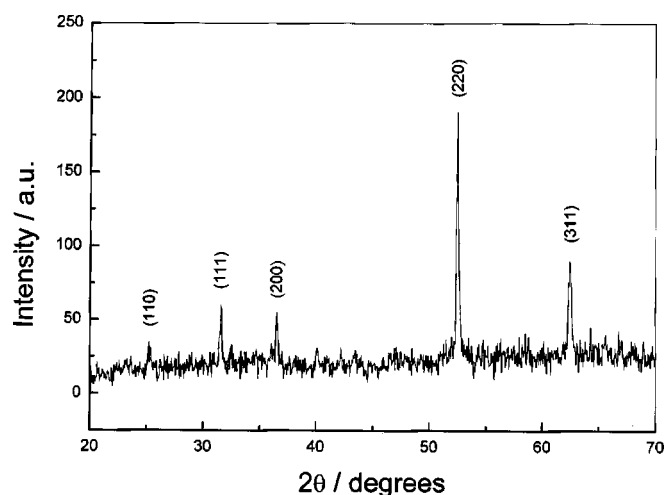

Figure 1. Powder XRD pattern of a tin oxide film coated by RTACRP.

with the O (1s) peak for commercially available SnO_2 powder sample at 531 eV. Binding energy values of Sn (3d$_{5/2,3/2}$) peaks for the coated tin oxide film are at 486.8 and 495.3 eV, respectively. These values are close to Sn (3$d_{5/2,3/2}$) peaks observed for the commercially available SnO_2 powder at 487 and 495.5 eV, respectively.[19] In both these samples, there was no charging. Peak width of Sn (3d$_{5/2}$) in the SnO$_x$ film was 2.6 eV compared to 2.3 eV observed for the commercially available SnO_2 powder. The difference between the Sn (3d) core level binding energy in SnO and SnO_2 is less than 0.2 eV and, hence, it is difficult to distinguish SnO_2 from SnO from the XPS study. Generally, films of single-
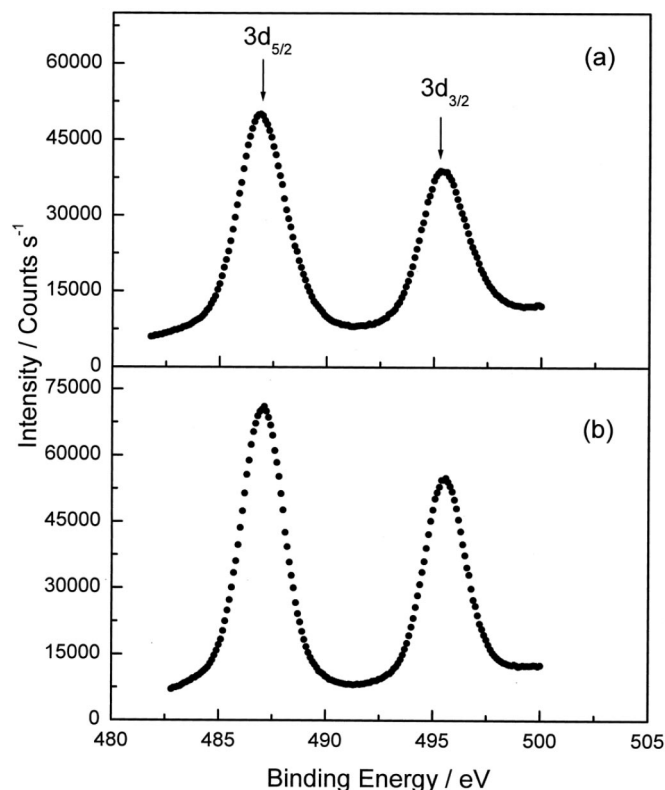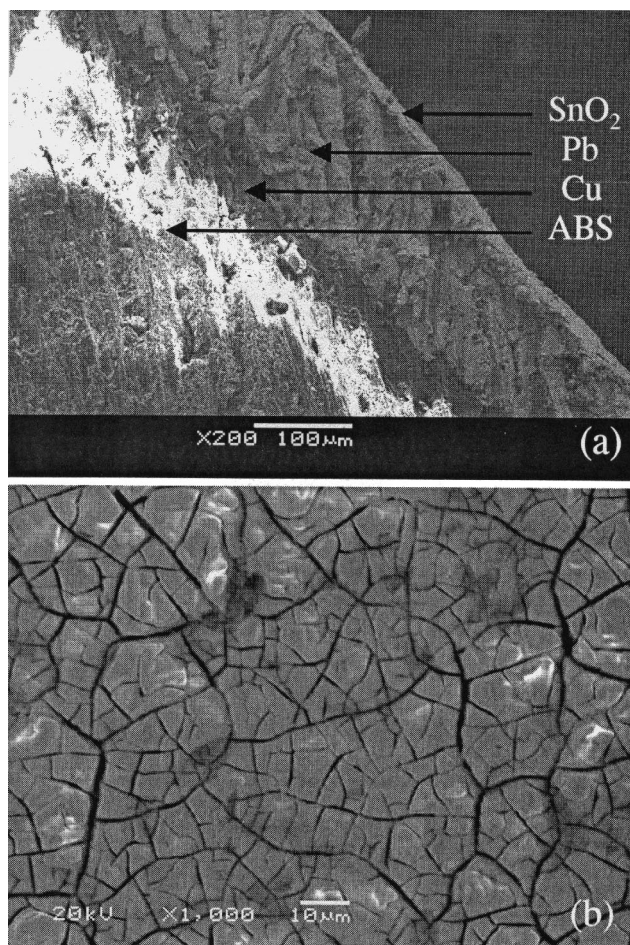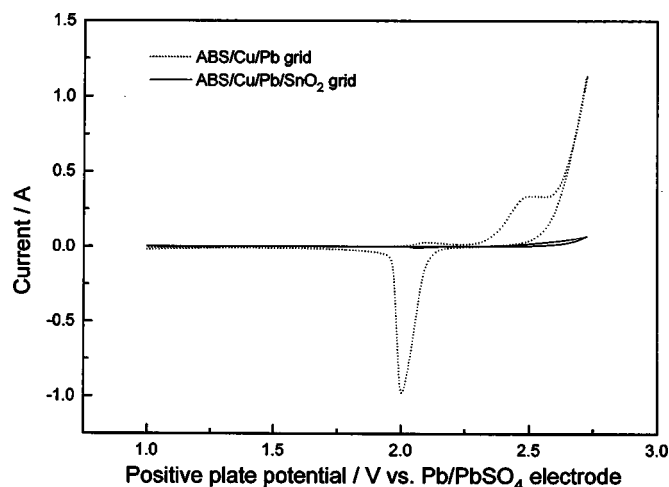

Figure 2. Sn (3d$_{5/2,3/2}$) XPS data for (a) tin oxide film obtained by RTACRP, and (b) commercially available SnO_2 powder.
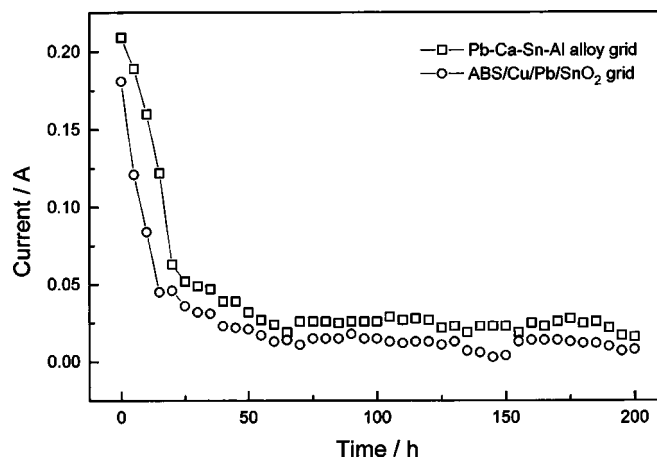
Figure 3. Electron micrographs depicting (a) cross-sectional and (b) surface morphologies of the ABS/Cu/Pb/SnO$_2$ grid.

Figure 5. Potentiostatic corrosion data for positive grids at a charging voltage of 2.5 V at 55°C.

phase materials show a narrower linewidth, and observation of higher widths of Sn core level in the film suggests the presence of both Sn^{2+} and Sn^{4+} species. The peak width can also be greater owing to the conducting nature of the film. XPS study thus indicates the presence of a conducting SnO$_2$-like phase.

Figure 3a shows the cross-sectional SEM of the grid. We clearly see the respective layers of ABS, Cu, Pb, and SnO$_2$. The SEM of the SnO$_2$ film shown in Fig. 3b suggests the SnO$_2$ film to be surface-cracked. The CV of ABS/Cu/Pb and ABS/Cu/Pb/SnO$_2$ grids in the potential range between 1 and 2.7 V *vs.* Pb/PbSO$_4$ electrode are shown in Fig. 4. The cyclic voltammetry data for the ABS/Cu/Pb grid show distinct peak currents at 2 V *vs.* Pb/PbSO$_4$ electrode, due to the conversion of PbO$_2$ to PbSO$_4$ and, at 2.5 V *vs.* Pb/PbSO$_4$ electrode, due to conversion of PbSO$_4$ to PbO$_2$. By contrast, we observe suppression of these peak currents in the CV for the ABS/Cu/Pb/SnO$_2$ grids, suggesting a substantial reduction in lead corrosion from the grids. Since corrosion is a limiting factor for the performance of the lead-acid batteries, we have conducted potentiostatic corrosion studies on the positive grids at a cell voltage of 2.5 V in flooded electrolyte (1.28 specific gravity aq H$_2$SO$_4$) configuration at 55°C, and the data are shown in Fig. 5. The data show lesser corrosion rate for the ABS/Cu/Pb/SnO$_2$ grids in relation to conventional Pb-Ca-Sn-Al alloy grids. The corrosion rates obtained from the weight loss method for ABS/Cu/Pb/SnO$_2$ and Pb-Ca-Sn-Al alloy grids are 9×10^{-3} and 22×10^{-3} g/cm^2/day, respectively. After confirming the stability of the ABS/Cu/Pb/SnO$_2$ grids in aq H$_2$SO$_4$, the grids were pasted with active material so as to form a 6 V/1 Ah lead/acid battery. The ohmic-drop experiments conducted on ABS/Cu/Pb/SnO$_2$ and Pb-Ca-Sn-Al alloy grids yield comparable values, suggesting ABS/Cu/Pb/SnO$_2$ grids to be appropriate for use in lead/acid cells.

**Figure 4.** CVs of ABS/Cu/Pb and ABS/Cu/Pb/SnO$_2$ grids.
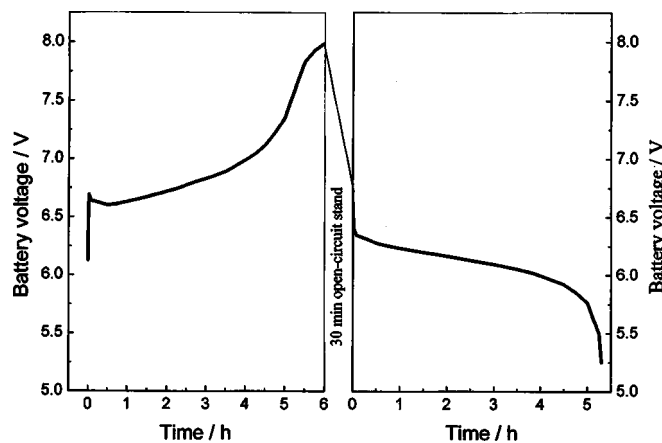
Figure 6. Typical C/5 rate galvanostatic charge-discharge data obtained at 25°C for the 6 V/1 Ah lead/acid battery.
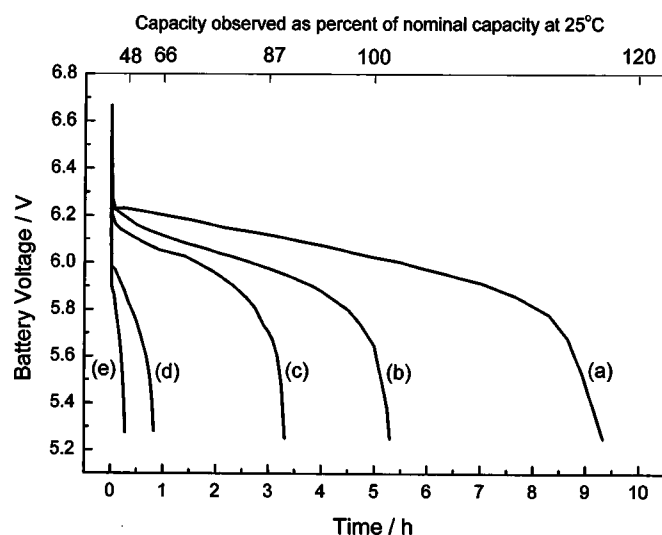
Figure 7. Performance characteristics of the 6 V/1 Ah lead/acid battery obtained at 25°C for (a) C/10, (b) C/5, (c) C/3, (d) C, and (e) 3C discharge rates.

The 6 V/1 Ah battery was subjected to about three formation cycles, and a typical galvanostatic charge-discharge data for the battery obtained at 25°C and at 5 h rate (C/5 rate) are shown in Fig. 6. The data suggest a faradaic efficiency of about 88% for the battery. The electrodes were not soaked in aq H_2SO_4 prior to their formation charging, as tin oxide tends to dissolve in aq H_2SO_4 below 0.5 V *vs.* Pb/PbSO$_4$ electrode.[8] Performance characteristics of the battery at different rates ranging between C/10 and 3C rates are shown in Fig. 7. As expected, the battery exhibited an increase in capacity of about 20% at C/10 rate as compared to its capacity at C/5 rate; at discharge rates higher than C/5 rate, the battery capacity decreased monotonically. Figure 8 shows the discharge data at different temperatures between 50 and −30°C. As seen from the data in Fig. 8, the battery exhibited a 10% increase in its capacity at 50°C as compared to its capacity observed at 25°C. At temperatures below 25°C, the capac-
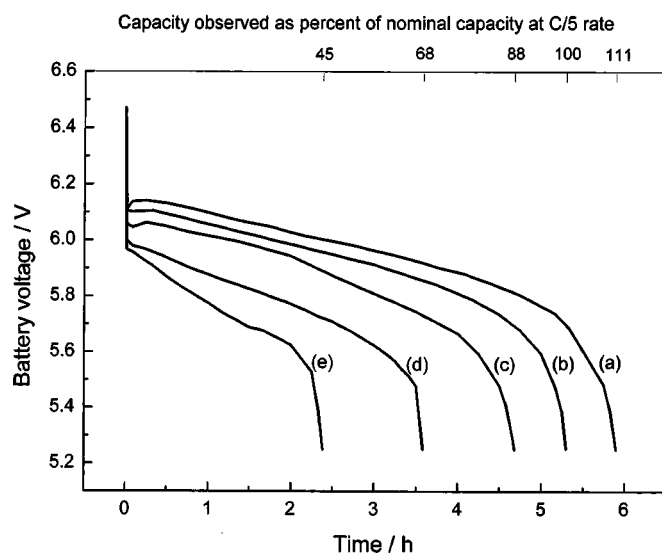
Figure 8. Effect of temperature on the discharge capacities of the 6 V/1 Ah lead/acid battery obtained for C/5 rate at (a) 50, (b) 30, (c) 10, (d) −10, and (e) −30°C.
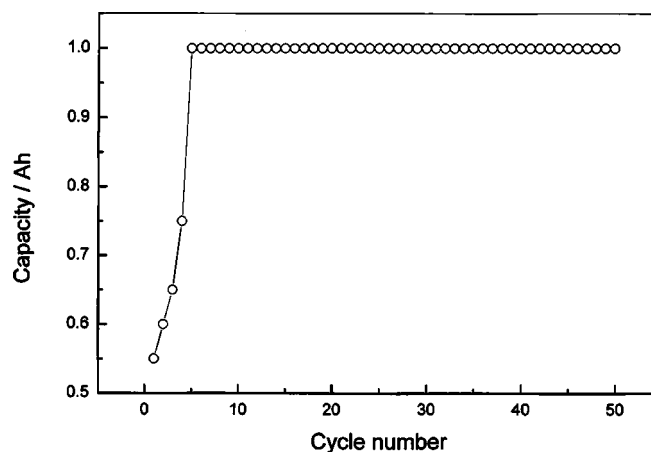
Figure 9. Cycle-life data for the 6 V/1 Ah lead/acid battery obtained at C/5 rate at 25°C.

ity values of the battery decreased with temperature. The battery was finally charged and discharged at C/5 rate for over 50 cycles at 25°C and the data summarized in Fig. 9 show little deterioration in the performance of the battery.

Conclusions

By employing a rapid thermally activated chemical reaction process (RTACRP), it has been possible for the first time to coat lightweight plastic grids for lead/acid batteries with an acid-resistant coating of conductive tin oxide. RTACRP is a far-from-equilibrium process, which probably accounts for the formation of conductive tin oxide coating at a relatively low temperature. The tin oxide-coated grids can be used to produce positive and negative plates for lead/acid batteries. The use of lightweight grids promises to push the energy density of lead/acid batteries beyond 50 Wh/kg.

References

1. D. A. J. Rand, R. Woods, and R. M. Dell, *Batteries for Electric Vehicles*, p. 99, Research Studies Press, Baldock, Hertfordshire, U.K. (1998).
2. T. C. Dayton and D. B. Edwards, *J. Power Sources,* **85**, 137 (2000).
3. R. H. Hammar and D. J. Harvey, U.S. Pat. 4,221,854 (1980).
4. N. Pinsky and S. A. Alkaitis, U.S. Pat. 4,713,306 (1987).
5. J. J. Rowlette, U.S. Pat. 5,643,696 (1997).
6. K. Tsuchida and H. Imai, U.S. Pat. 6,232,017 (2001).
7. J. B. Timmons, R. Bhardwaj, and J. A. Orsino, U.S. Pat. 6,316,148 (2001).
8. I. Kurisawa, M. Shiomi, S. Ohsumi, M. Iwata, and M. Tsubota, *J. Power Sources,* **95**, 125 (2001).
9. I. Kurisawa, M. Shiomi, S. Ohsumi, M. Iwata, and M. Tsubota, *GS News,* **59**, 7 (2000).
10. J. B. Timmons, J. A. Orsino, and R. Bhardwaj, U.S. Pat. 6,447,954 (2002).
11. R. C. Bhardwaj and J. Than, *J. Power Sources,* **91**, 51 (2000).
12. G. Barkleit, A. Grahl, M. Maccangi, M. Olper, P. Scharf, R. Wagner, and H. Warlimont, *J. Power Sources,* **78**, 73 (1999).
13. P. T. Moseley and R. D. Prengaman, *J. Power Sources,* **107**, 240 (2002).
14. J. Wang, H. K. Liu, S. X. Dou, S. Zhong, Y. Zhu, and C. Fu, *J. Power Sources,* **113**, 241 (2003).
15. D. R. Battlebury, *J. Power Sources,* **80**, 7 (1999).
16. K. R. Bullock, *J. Power Sources,* **116**, 8 (2003).
17. S. A. Shivashankar, A. K. Shukla, A. U. Mane, B. Hariprakash, and S. A. Gaffoor, U.S. Pat. Appl. (2003).
18. W. Losocha and K. Lewinski, *J. Appl. Crystallogr.,* **27**, 437 (1994).
19. *Practical Surface Analysis*, D. Briggs and M. P. Seah, Editors, p. 505, John Wiley & Sons, New York (1984).