Evaluation of Carbon Fiber as An Additive for A Cureless Positive Plate in Valve-regulated Lead-acid Batteries

J. Wang\textsuperscript{ab}, Z.P. Guo\textsuperscript{ab}, G.X. Wang\textsuperscript{ab}, S.Y. Chew\textsuperscript{ab}, and H.K. Liu\textsuperscript{ab}

\textsuperscript{a} Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia.
\textsuperscript{b} ARC Centre of Excellence for Electromaterials Science, University of Wollongong, NSW 2522, Australia.

A new plate manufacturing technique has been developed for the VRLA lead-acid battery. The plates were fabricated by using pure lead oxide as a starting material to replace conventional leady oxide. The plates can be assembled directly into a battery case after pasting, and then a case formation can be performed directly, without the plates undergoing the conventional curing process. The effect of carbon fiber as an additive for the positive plate prepared using pure lead oxide has been evaluated.

1. Introduction
The effects of additives, including graphite, needle coke, glass microspheres, and carbon fiber, on material utilization and the cycle life of positive plates in lead-acid batteries have been reported previously [1-2]. One common effect of all these additives is to increase the porosity and the BET (Brunauer-Emmett-Teller) surface area of the positive plate, providing a better balance between the positive active material and the electrolyte in and near the positive plate. We have previously reported a novel plate making process that requires no curing [3-4]. This new process has demonstrated many advantages over the conventional process, including simplification of the manufacturing process, a short production time, and low cost. This study aims to evaluate the effect of carbon fiber as an additive for positive plates prepared with pure lead oxide using the non-curing process.

2. Sample preparation
Pure lead oxide (Aldrich) was blended with 0.25-0.75 wt.% carbon fiber and mixed with 1.4 (sp.gr.) sulfuric acid and water to prepare a positive paste with 4.0 g cm\textsuperscript{-3} wet density. The positive plates were made by applying the paste on lead-coated glass fiber grids 25 mm \times 20 mm \times 1.2 mm in size. The plate weight was 5 g/plate.

All the plates were made without any conventional curing processes. The test cell was constructed with one positive plate and two commercial negative plates with a separator in between. The cells were filled with an electrolyte of H\textsubscript{2}SO\textsubscript{4} (1.25 sp.gr.). The cell formation was applied at a constant current density of 25 mA g\textsuperscript{-1} for 24 hours. A discharge test was conducted with discharge currents of 20, 50, 100, and 200 mA g\textsuperscript{-1} at different temperatures. Cycle life testing was performed at a constant current of 25mA g\textsuperscript{-1} for both the charge and discharge at 25\degree C. During the charge, the cut-off voltage was set at 2.45V, and then charging was maintained at constant voltage until 110\% of the previous discharge capacity was reached. The BET surface areas of the formed positive pastes with different amounts of carbon fiber were measured with a NOVA 1000 high-speed gas absorption analyzer (Quantachrome Corporation, USA). Sample degassing prior to the measurement, was carried out under vacuum at 120\degree C for 20 h. The morphology of the carbon fibers was examined with a scanning electron microscope (SEM, Leica, 440).
3 Results
3.1 Effect of the BET Surface Area on Material Utilization

Fig.1(a) shows the relationship between the amount of carbon fiber and the utilization of the positive active mass (PAM). Note that the material utilization increased when carbon fibers were added to the PAM at all the discharge rates. The material utilization increased with the carbon fiber loading until a maximum was attained at approximately 0.5 wt.% carbon fiber. When the utilization of the PAM was plotted against its BET surface area, a linear relationship was obtained between both factors at all discharge rates. Accordingly, the increase in utilization of the positive active mass can be related to the increase in its BET surface area. Therefore, the beneficial effects on material utilization with addition of carbon fiber can be attributed to the increase in BET surface area of the plate (Fig. 1(b)).

Fig.1 (a) Relationship between the amount of carbon fiber and the utilization of the positive active material. (b) Relationship between BET surface area and utilization of PAM.

3.2 Influence of Temperature on Material Utilization

Fig. 2 shows the influence of the temperature on the positive material utilization for plates with various carbon fiber contents. The four curves are given as percentage of positive material utilization versus the temperature at one fixed rate of discharge, 50 mA g\(^{-1}\). The general trend is that the material utilization declines as the temperature goes down. This trend becomes more pronounced at temperatures below the freezing point of water. Low temperatures raise the internal resistance and cause increased polarization. The effect of addition of carbon fiber on utilization at various temperatures can be seen clearly from Fig. 2. Below 0 °C, a significant improvement in utilization can be obtained with a higher level of carbon fiber content (over 0.5wt.%). This beneficial effect can be attributed to reduction of the kinetic hindrance, which makes a larger part of the material available, a capacity that would normally remain unused at lower or no carbon fiber addition.

3.3 Cycle Life

The discharge capacity vs. the cycle number is shown in Fig. 3. The carbon fiber in the pastes increases the capacity of the positive active material during the initial cycles. As the cycles proceeded, the capacity declined sharply for cells with higher additions of carbon fiber. Similar phenomena have been reported previously [2]. The detrimental effect on the cycle life can be attributed to the presence of carbon fiber, which weakens binding forces in the active material during cycling. The discharge capacity vs. the cycle number is shown in Fig. 3.
Fig. 2 Influence of temperature on positive material utilization with different carbon fiber contents at a discharge rate of 50mAg\(^{-1}\).

Fig. 3 Discharge capacities vs. cycle number with various carbon fiber contents.

**Acknowledgments**

This work was financially supported by the Australian Research Council under an ARC-SPiRT project (C89805127). The authors also thank Dr. T. Silver for critical reading of the manuscript.

**References**