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THE POSSIBLE USE OF MODIFIED TITANIUM AS POSITIVE GRID IN LEAD-ACID BATTERIES

Chiaki IWAKURA, Meguru INAI, and Hideo TAMURA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadakami, Suita, Osaka 565

During the course of studying on DSA-type electrodes, it was found that the ruthenium dioxide coated titanium has a promising character as a positive grid in lead-acid batteries. This paper briefly describes the preliminary works.

In modern lead-acid batteries, lead alloys are exclusively used as a grid material. However, the corrosion of positive grids is a fundamental problem of battery operation that produces many undesirable effects. Titanium has very useful properties such as an excellent corrosion resistance, a high mechanical strength and a light weight. Therefore, it has been suggested as a substitute for lead as a grid material by Cotton and Dugdale.(1) They claimed that the platinum coating was necessary to prevent the passivation of titanium positive grid during the charge-discharge processes. However, the use of a more favorable coating material which easily forms a solid solution with titanium dioxide can be expected to improve the characteristic of the titanium positive grid in a manner acting to reduce passivation. In the present work, ruthenium dioxide was adopted as a coating material because all of TiO_2 (rutile), RuO_2 and β-PbO_2 have a rutile-type structure. The ruthenium dioxide coating was accomplished by thermal decomposition of ruthenium trichloride on a smooth titanium sheet ($2.54 cm^2$).(2) The detail of the preparative procedure was described elsewhere.(3) The amount of RuO_2 loading was $10^{-7} mol/cm^2$ (i.e. calculated thickness: ca. 200Å). The resulting thin film of ruthenium dioxide was fairly effective for preventing the passivation of the titanium base.

A standard pasting procedure was employed in the preparation of positive plates. After pasting, the plate was formed in 1.050 sp gr H_2SO_4 prior to use. The geometric area of the plate exposed to the solution was reduced to $1 cm^2$ by using a Teflon holder. The rest potential of the Ti/RuO_2/paste plate obtained in this manner was +1.185V vs. Hg/Hg_2SO_4 in 1.290 sp gr H_2SO_4 at 25°C, while that of the pure lead electrode was -0.955V vs. Hg/Hg_2SO_4. Accordingly, the open-circuit voltage of the cell will be about 2.14V, which agrees with that for the usual lead-acid battery. Furthermore, the Ti/RuO_2/paste plate was stable against the anodic polarization, and gave the anodic Tafel line with the slope of 0.12V in 1.290 sp gr H_2SO_4. This value is in fair agreement with that reported for oxygen evolution on β-PbO_2 electrode,(4) but not on RuO_2 and Ti/RuO_2 electrodes.(5) From these facts, it has become apparent that the Ti/RuO_2 grid acts as an inert but conducting support during the charging of the positive plate.

Some preliminary tests of charge-discharge cycling were carried out by means of cyclic voltammetry. In such experiments, the potential was scanned between +0.75 and +1.65V vs. Hg/Hg_2SO_4 with the scan rate of 0.25mV/sec (2hr/cycle). These conditions are normal for the charge-discharge test of positive plates. For comparison with the Ti/RuO_2 grid, the pure lead sheet with the same size was also used as a positive grid. The voltammograms of the Ti/RuO_2/paste plate were similar to those of the Pb/paste plate, indicating that there was no significant difference in the ohmic resistance between the Ti/RuO_2 and Pb grids. The variations of discharging capacity with number of cycles are shown in Fig.1. It is evident from this figure that these two plates have approximately the same tendency of the change in capacity. The capacities decreased gradually with increasing the number of cycles, and finally led to a sharp decrease, mainly due to the shedding of the active material. The discharge efficiency of the Ti/RuO_2/paste plate was comparable to that of the Pb/paste plate. After these tests, the remaining active materials were removed and then the microscopic examination of the grid surface was conducted. The results indicated that the surface of the Ti/RuO_2 grid was unaltered while the Pb grid appreciably underwent a corrosion.

In order to retard the shedding of the active material, a plastic sheet having micropores6) was placed on the positive plate so that the sheet behaved like a glass fiber retainer mat prior to the forming of the plate. Using this type of plate, the charge-discharge tests were done under the same conditions as in the above mentioned tests, and the results are shown in Fig.2 as a plot of the discharging capacity against the number of cycles. Evidently, the service life of the positive plate was prolonged to a great extent. In this case, most of the active materials still remained on the grid surface even after cycled more than 150 times.

On the basis of these preliminary works, coupled with the other related data, it seems likely that the ruthenium dioxide coated titanium has a promising character as a positive grid in lead-acid batteries. Iridium dioxide and some other oxides may be substituted for ruthenium dioxide since they have also a rutile-type structure. In the use of long duration, however, the Ti/RuO_2 grid being developed in the present work may have some problems such as the lack of the adhesion of active material to the grid, the low oxygen overvoltage of the ruthenium dioxide layer and the development of an additional ohmic resistance at the Ti/RuO_2 interface. Therefore, much more information will be needed before one reaches to the final decision whether this kind of grid can be used in practice or not. Further work is now in progress.

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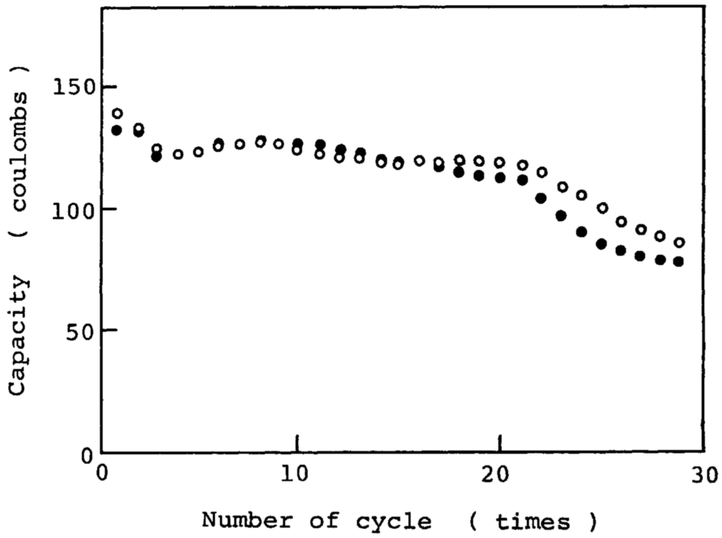

Fig.1 Variations of discharging capacity with number of cycles in 1.290 sp gr H_2SO_4

○: Ti/RuO_2(10^{-7}mol/cm^2)/paste(731mg/2.54cm^2)
●: Pb/paste(775mg/2.54cm^2)

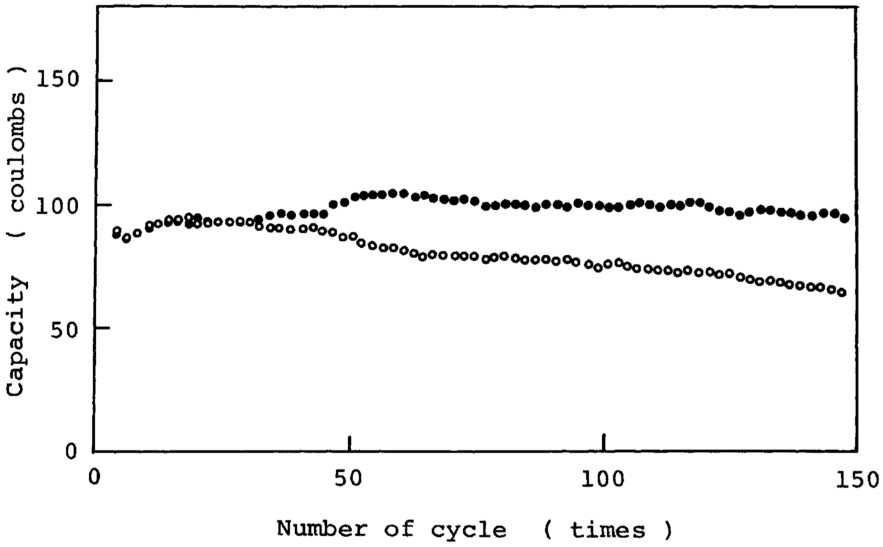

Fig.2 Variations of discharging capacity with number of cycles in 1.290 sp gr H_2SO_4

○: Ti/RuO_2(10^{-7}mol/cm^2)/paste(743mg/2.54cm^2)
●: Pb/paste(829mg/2.54cm^2)

References and Notes

1) J. B. Cotton and I. Dugdale, " Batteries, Research and Development in Non-Mechanical Electric Power Sources, Proceedings of the 3rd International Symposium," Ed. by D. H. Collins, Pergamon Press, New York, N.Y., 1963, pp. 297-307.

2) For practical use, a sandblasted titanium base should be used in place of the smooth titanium sheet in order to produce a good adhesion of the oxide layer to the base and the least electrical interface resistance.

3) W. O'Grady, C. Iwakura, J. Huang, and E. Yeager, " Proceedings of the Symposium on Electrocatalysis," Ed. by M. W. Breiter, The Electrochemical Society, Princeton, N.J., 1974, pp. 286-302.

4) P. Rüetschi and B. D. Cahan, J. Electrochem. Soc., 105, 369(1958).

5) C. Iwakura, K. Hirao, and H. Tamura, Electrochim. Acta, 22, 335(1977).

6) " Yumicron " supplied from Yuasa Battery Co. Ltd. (thickness: 0.1-0.2mm, electrical resistance: 0.0002-0.0004Ω/dm^2, mean pore diameter: 0.1-1μm, porosity: 60%).

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