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SHORT COMMUNICATION

Application of SEM for monitoring morphological changes on the surface of secondary cell electrodes during cycling

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A method for observing a specific region of an electrode during its lifetime is described, enabling morphological changes on the electrode surface to be monitored. The use of the present method is briefly illustrated using as an example a sintered cadmium electrode in an alkaline medium.

Many changes occur within secondary cell electrodes during cycling, for example, growth and dissolving of crystals, etc. These changes have been observed by a number of authors using various techniques, *inter alia* by means of both light and scanning electron microscopy [1–3]. Also in the course of our studies [4, 5] of phenomena determining the service life and reliability of sintered cadmium electrodes a consideration of morphological changes of the electrode active mass proved to be necessary. Besides some commonly used techniques (for example measurements of electrochemical properties of electrodes, changes in the value of specific surface area, chemical composition, free pore volume, observations of active mass migration, microscopic observations of electrode cross-sections, etc.) an exploitation of scanning electron microscopy was found to be very useful. In order to be able to evaluate more precisely the course of the above-mentioned processes on the electrode surface, i.e. to observe a specific region of the surface during the whole electrode lifetime (for example an individual crystallite of the active mass) and thus to eliminate in part, the necessity of a statistical approach to observed phenomena (as is the case when interpreting common micrographs of a randomly chosen area of the electrode), we have developed a new experimental technique, which is described in the following paragraphs.*

Model cells of the electrodes under investigation were assembled, enabling the removal of the cadmium electrode at a pre-determined stage of its lifetime, the performance of necessary microscopic observations on it, and afterwards re-assembly of the cell. The electrodes used were circular plates 23 mm in diameter and 0·75 mm thick; they were washed and dried before measurement by a standard procedure. Observations were performed on totally discharged electrodes. The above-mentioned method may be modified in various ways, however, for example if certain experimental conditions are fulfilled (preventing oxidation during washing and drying) it is also possible to observe charged electrodes with good results. A system of two rectangular coordinate axes was used for finding the identical region for examination. The axes were marked mechanically on the surface of the sintered plate. The coordinate system must be as accurate as possible (sharp lines) and stable during the impregnation and cycling processes. However, other methods of finding the identical region may be used as well. This system was used in order to always obtain an identical orientation of the specimen image on the scanning electron microscope monitor. It was then possible to find the identical region of the electrode with fairly good precision, using micrometric displacement of the specimen pedestal, even

* As has been pointed out by the referee, a similar technique has been previously reported [6].

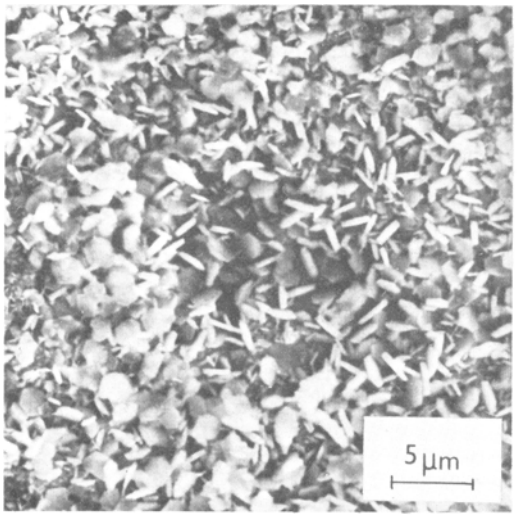

Fig. 1. Detail of electrode surface after 2 cycles.

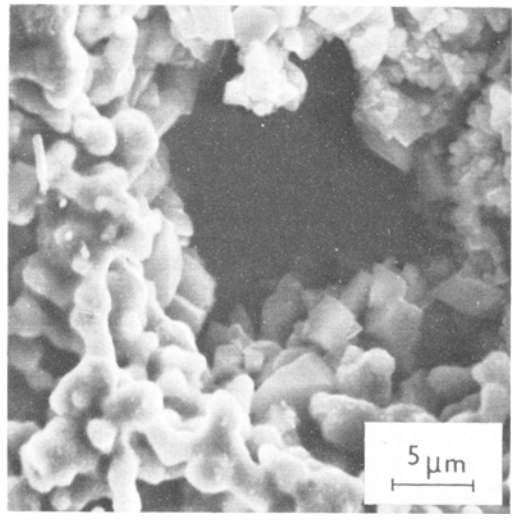

Fig. 3. Detail of electrode surface after 250 cycles.

if its appearance was substantially changed after operations carried out since the preceding observation. In order to prevent a perturbation of the electrochemical system during cycling, the electrodes were not stuck to the specimen holder with a conductive glue and no metal was evaporated on their surface, as is otherwise common in scanning electron microscopy. This fact caused a lower quality in the micrographs obtained in several cases, but even these photographs may be used for observing the changes on the electrode surface with good results. No example of beam damage was observed.

For an illustration of the applicability of the present technique see Figs. 1–4, which are micrographs of the changes on the surface of one of the electrodes investigated (at a constant magnification). Large crystals of the active mass are being formed on the surface instead of the original small crystallites during cycling and the surface of the sintered plate becomes observable; the crystals in the surface layer are dissolving and/or falling off, while the size of the crystals in the lower layer is steadily increasing. Several details were observed on each electrode at several magnifications, always on both sides of the electrode. Results obtained by

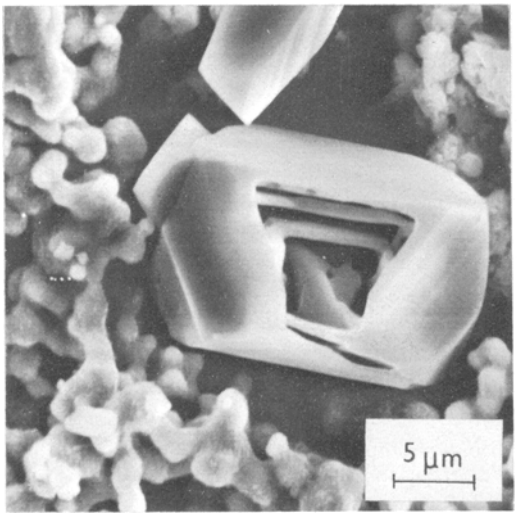

Fig. 2. Detail of electrode surface after 112 cycles.

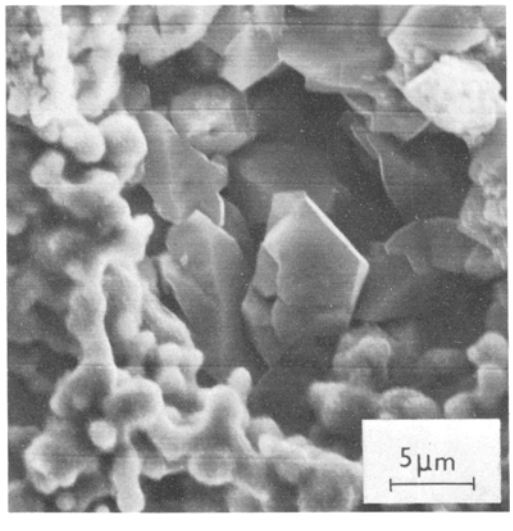

Fig. 4. Detail of electrode surface after 419 cycles.

means of the above-described procedure may be usefully combined with results of other physico-chemical measurements. The results of our investigations have been already described in part [4, 5]; a summary of total results and their technological applications will be published later in this Journal.

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References

[1] R. Barnard, G. S. Edwards, J. A. Lee and F. L. Tye, *J. Appl. Electrochem.* **6** (1976) 431.
[2] A. C. Simon, S. M. Caulder and J. T. Stemmle, *J. Electrochem. Soc.* **122** (1975) 461.
[3] J. L. Weininger and C. R. Morelock, *ibid* (1975) 1161.
[4] J. Marek, Thesis, Technical University Brno (1977).
[5] J. Marek, I. Mohyla and M. Stompfe , 28th meeting of ISE, Extended Abstracts II, 397, Varna, September (1977).
[6] S. Hattori. M. Yamaura, M. Kohno, Y. Ohtani, M. Yamane and H. Nakashima, 'Power Sources 5', p. 139. Proc. 9th Int. Power Sources Symp. 1974 (ed. D. H. Collins) Academic Press (1975).