CURRENTLESS PASSIVATION OF THE PbO_2 ELECTRODE WITH RESPECT TO THE INFLUENCE OF TIN

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During currentless storage (*i.e.*, open circuit), the corrosion layer of the PbO_2 electrode undergoes changes that result in a considerable potential drop across the corrosion layer during subsequent discharge. This is observed especially after high-temperature drying (>100 °C) or after storage for a long time with, and without, electrolyte [1 - 12]. The principal characteristics of the galvanostatic discharge curves are shown in Fig. 1.

The change in the corrosion layer consists mainly of a reduction in the instability from the thermodynamic point of view. This has been produced during the anodic phase by a reduction in the oxygen gradient between the grid lead and the PbO_2 of the active mass. In turn, this causes a broadening of the PbO_n-zone ($1 \leqslant n < 1.5$) and imparts semiconducting properties to the electrode [6, 7]. The reduction of the oxygen gradient is brought about by a solid-state reaction, and by a liquid-state reaction when there is a deficiency of acid. The products of both reactions are PbO and PbO_n. The reactions are shown schematically in Fig. 2.

The non-ohmic properties and the potential- and polarity-dependence of the resistance of the electrode are illustrated in Fig. 3 (curves 7, 8) by potentiodynamically generated voltage/current curves at passivated dry-charged PbO_2 electrodes. The origin of the passivation must be located in the corrosion layer because plots across the active mass show clear ohmic properties (curves 1 - 4). The passivation of the PbO_2 electrode is avoided in the case of drying and storage by plating the grid of the electrode with a tin layer [13]. This is demonstrated by curves 5 and 6 in Fig. 3, and by the data of Fig. 4 (galvanostatic discharge curves after drying) and Fig. 5 (galvanostatic discharge curves after storage).

Impedance methods have been used to characterize the passivation layer. For dried electrodes, it has been found that the passive layer contains a capacity component in addition to the non-linear part of the resistance. Oscillographic observations of the a.c.-potential properties of the passivated PbO_2 electrode have allowed the cause of passivation to be explained in terms of a phase-junction model. On one side, a Schottky barrier is formed between the metallic lead and the p-conducting PbO_n, while on the other side a

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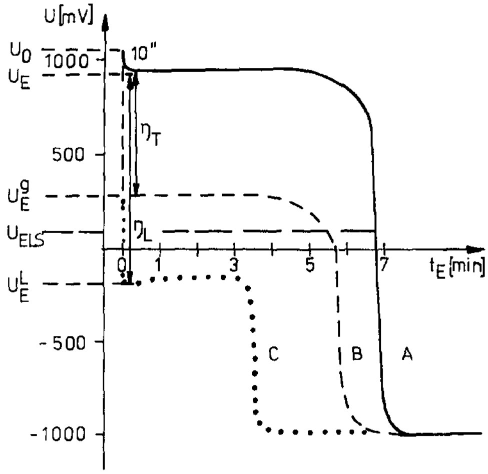


Fig. 1. Typical galvanostatic discharge characteristics of PbO_2 electrodes. A, after formation; B, after drying (175 °C, 2 h); C, after storage.

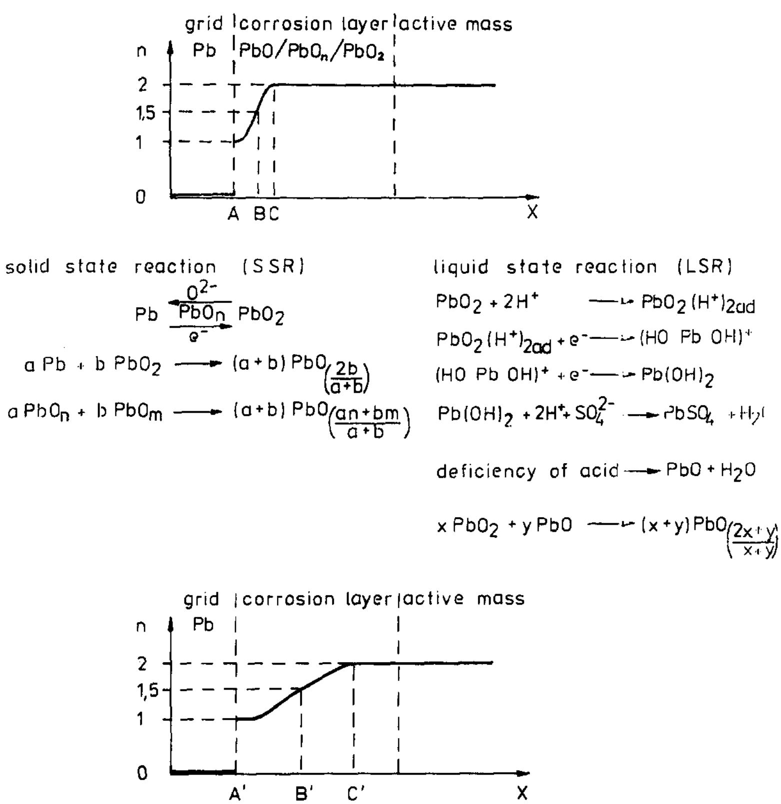


Fig. 2. Change in corrosion layer during passivation processes.

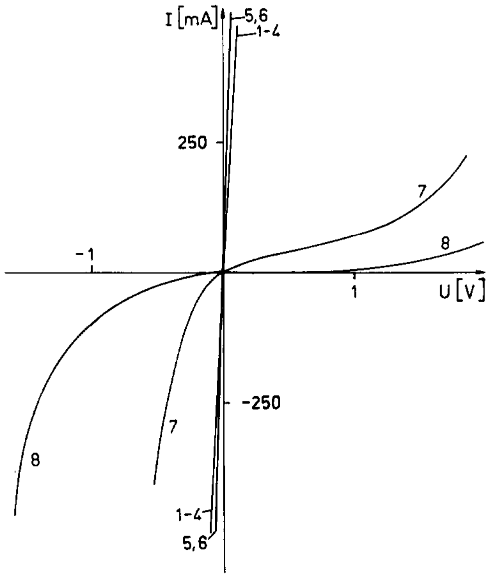


Fig. 3. Voltage/current curves of dried PbO_2 electrodes measured across active mass (curves 1 - 4) and between grid (Pb–2.5%Sb) and active mass (curves 5 - 8). Curves 1, 5, Sn-covered grid, dried at 80 °C; curves 2, 6, Sn-covered grid, dried at 175 °C; curves 3, 7, dried at 80 °C; curves 4, 8, dried at 175 °C.

pn-junction develops between the p-conducting PbO_n and the n-conducting PbO_2 [14]. Because of the close vicinity of the two phase junctions, it is reasonable to assume that an npn-transistor structure is set up with a base that is not freely accessible. This configuration has been modelled and, as a result of the non-ideal structure of the real semiconductor junctions of the passivated PbO_2 electrode, an additional connection of the

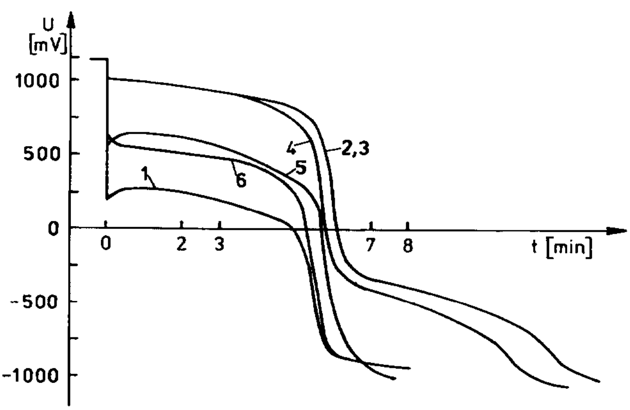
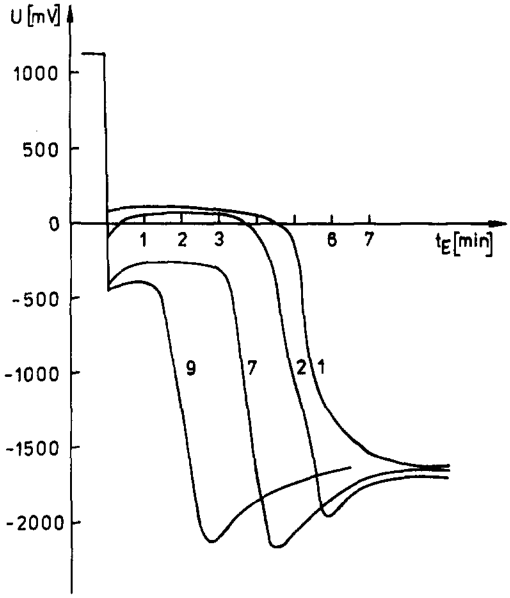
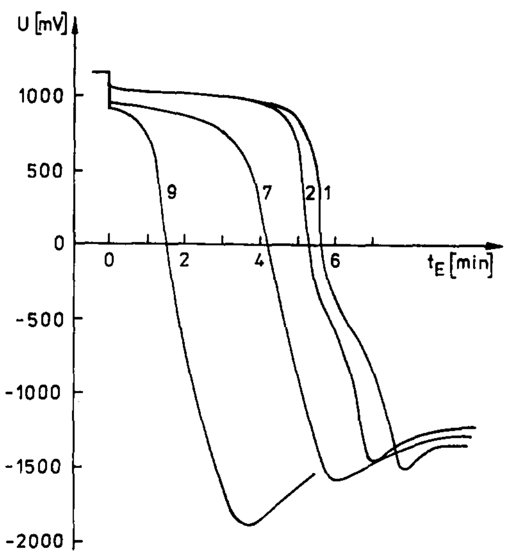


Fig. 4. Galvanostatic discharge curves of dried PbO_2 electrodes with different modified grids ($T = 175$ °C; $I \triangleq 3 \times C_{20}$). 1, Pb–2.5%Sb; 2, grid covered with 3 μm Sn; 3, grid covered with 1.5 μm Sn; 4, Pb–2.5%Sb–1%Sn; 5, Pb–2.5%Sb–0.1%Sn; 6, Pb–2.5%Sb, Sn species adsorbed.



(a)



(b)

Fig. 5. Galvanostatic discharge curves after wet storage at 40 °C ($I \triangleq 3 \times C_{20}$): (a) Pb–2.5%Sb; (b) Pb–2.5%Sb covered with 3 μm Sn. Number on each curve represents storage time in months.

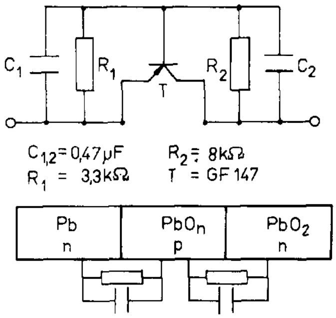


Fig. 6. Representation of the phase junctions of a passivated PbO_2 electrode and a modelled equivalent circuit.

modelled semiconductor junctions to a parallel *RC*-combination has been established (Fig. 6).

The failure of a passivation layer to form in the presence of tin species is obviously due to a high doping of PbO_n by the tin. Clearly, the doped PbO_n has a considerably higher conductivity, and possibly even exhibits a switch in conductivity, than that of an n-type semiconductor. Thus, the semiconductor junctions metal/PbO_n and PbO_n/PbO_2 take on an ohmic character in the presence of tin.

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