

Figure 18.19 Cross-section of a negative flat-plate electrode after 3.5 years of operation in a photovoltaic system. The sections were taken from the upper, central and lower parts of the electrode (from left to right, respectively). Sulphation is clearly indicated in the lower section by the very coarse pores between large crystals, and by the noticeable broadening of the electrode, due to the difference in the specific volumes of Pb and PbSO₄ (Photo source: ZSW)

18.4.7.4.3 Corrosion

The high positive potential at the positive electrode results in the corrosion of the lead grid [24]. On one hand, this causes the cross-section of the grid to decrease, so that the grid resistance increases. On the other hand, a layer consisting of lead dioxide, lead oxide and lead sulphate forms between the grid and the active material, which also raises the contact resistance. This becomes evident during charging and discharging as an increased ohmic voltage drop. Figure 18.20 shows the cross-section of a tubular electrode from a battery after 3.5 years of operation. The lead core (grid rod in the centre of the tube) has almost completely disappeared due to corrosion.

The corrosion rate depends on the acid density, the electrode potential, the temperature, the grid alloy, the active material coverage [25] and a most important factor, the manufacturing quality of the grid. Corrosion is particularly pronounced for cell voltages below 2.0 V and above 2.4 V [24]. Corrosion is minimal for cell voltages around 2.23 V. Corrosion is an irreversible ageing effect and increases the internal resistance of the battery. An indirect consequence is that the current distribution becomes more inhomogeneous in the vertical direction, so that sulphation is accelerated in the lower parts of the electrodes. In batteries for PV systems, thicker grids are used to reduce the effect of corrosion and thus extend the lifetime.

18.4.7.4.4 Erosion

Both electrodes are subjected to strong mechanical loads during cycle operation. The reason is that up to 50% of the active material is converted to lead sulphate during discharge. Lead sulphate has a volume per mole, which is 1.94 times larger than lead dioxide and 2.4 times larger than lead.