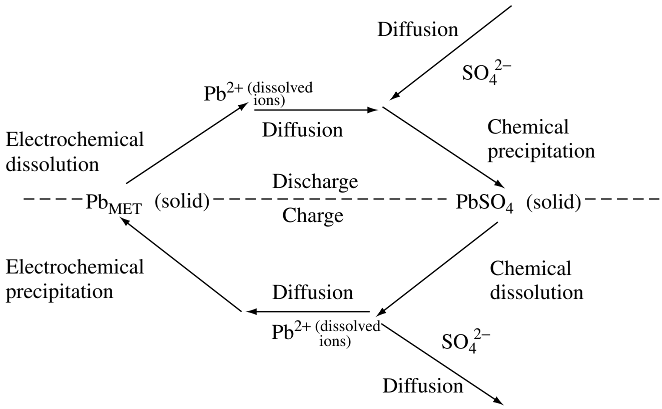

Figure 18.10 Schematic of the charge/discharge process in the lead electrode of a lead acid battery

away from the reaction surface. As the charged ions unbalance the number of positive and negative ions in the electrolyte, negatively charged ions are necessary to counterbalance the positive surplus. They are provided as ${SO_4}^{2-}$ ions from the sulphuric acid electrolyte. The ${SO_4}^{2-}$ ions are transported by diffusion from the free electrolyte volume to the reaction site of the electrochemical reaction. There, the Pb^{2+} and the ${SO_4}^{2-}$ ions meet and form $PbSO_4$ by a chemical precipitation process. This finally results in the formation of $PbSO_4$ crystals.

During charging, the reverse process takes place. Pb^{2+} ions are taken from the electrolyte to form solid Pb during the electrochemical precipitation process. These ions are transported by diffusion processes to the reaction site. To stabilise the Pb^{2+} ion concentration in the electrolyte, a chemical dissolution process of the $PbSO_4$ crystals takes place. Because the positive ions are removed from the electrolyte through the electrochemical precipitation process, the ${SO_4}^{2-}$ ions need to be transported away from the reaction site to assure electrical neutrality.

All these processes cause overvoltages.

1. Electrochemical dissolution with respect to precipitation described by the Butler–Volmer equation.
2. Transport of Pb^{2+} ions described by the diffusion law resulting in diffusion overvoltages.
3. Transport of ${SO_4}^{2-}$ ions described by the diffusion law, law of migration of charged ions in an electrical field and fluid dynamics caused by the change in the pore volume during charging and discharging resulting in diffusion overvoltages.
4. Chemical precipitation or dissolution of the $PbSO_4$ crystals forced by deviations of the ion concentration in the electrolyte from the equilibrium concentration resulting in concentration overvoltages.

All processes depend on the temperature. Further, the processes depend on the electrolyte concentration. The concentration influences the equilibrium current density of the Process 1, the diffusion rate of ions in Processes 2 and 3 and it has a strong impact on the