of the lead electrode, dissolved Pb^{2+} ions form the lead sulphate crystals ($PbSO_4$) with $SO_4{}^{2-}$. The rate of formation of sulphate crystals (and the dissolution of the crystals during charging) determines the concentration of the charged ions in the electrolyte and therefore the concentration overvoltage. The rate of forming and dissolving of sulphate crystals depends strongly on the crystal size, shape and number. These parameters depend on the operating conditions of the battery and on the ageing of the active material. Therefore, battery ageing and active material structure is reflected by the values of the concentration overvoltage and the charge-transfer overvoltage.

The diffusion overvoltage describes the transport of ions that are available in sufficient volume (in the lead acid battery these are the $SO_4{}^{2-}$ ions), thus a classical transport phenomenon. The concentration overvoltage describes the generation with respect to the absorption of ions from a chemical process.

Chemical processes are always driven by concentration gradients. Electrochemical processes are driven by the external currents. Therefore, the electrochemical process must take place exactly at the rate given by the external current. The rate of the chemical process depends only on ion concentration. With respect to the charge/discharge process in a battery, this means that the electrochemical process follows without delay any changes in the external current flow. Chemical processes have time constants as the rate of the process depends on the concentration in the electrolyte. In steady-state charge and discharge conditions, the rates of the electrochemical process and the chemical process need to be equivalent. This means that the ratio of the ion concentration and the equilibrium concentration in the electrolyte is constant.

All processes strongly depend on the temperature. The temperature dependence of the reaction rate k of a chemical reaction is described by the Arrhenius equation (C is a constant, E_A the activation energy).

$$k = C \cdot \exp\left(-\frac{E_A}{R \cdot T}\right)$$

The activation energy for many processes is of the order of 50 kJ/mole. From this experience, the rule of thumb "*increase of temperature by 10 K increases the reaction rate by a factor of 2*" is derived.

18.2.2 Batteries with Internal and External Storage

Electrochemical accumulators convert electrical energy into chemical energy. The energy is stored in a chemical compound. In secondary electrochemical batteries, this process is reversible. During discharging, the chemical energy is converted back into electrical energy. Thus, the converters determine the charging and the discharging power and the storage determines the energy capacity of the systems. This principle concept is described in Figure 18.2.

In secondary electrochemical batteries with internal storage, the converter and the storage cannot be separated. The interface of the active material to the electrolyte is