Here, a distinction between the so-called redox-flow batteries in which salts are dissolved in liquid electrolytes and the hydrogen/oxygen storage systems based on the electrolyser and the fuel cell will be made.

The costs for the converters and therefore the power sizing are independent of the storage size. Therefore, these systems show an economy of scale concerning the energy storage. The larger is the storage, the lower are the specific storage costs. This makes the systems interesting for seasonal storage or other long-term storage applications.

18.5.1 Redox-flow Batteries

In redox-flow batteries, the active material is made from salts dissolved in a liquid electrolyte. The electrolyte is stored in tanks. As the solubility of the salts is typically not very high, the energy density is in the range of lead acid batteries. The electrochemical charge/discharge reactions take place in the converter, which determines the power of the system. Therefore, redox-flow batteries belong to the group of batteries with external storage. Redox-flow batteries were already under investigation for stationary applications in the 1970s and 1980s. An overview of these activities can be found in [28]. Owing to problems with the materials, the investigations were almost stopped but were again started in the last year.

Redox-flow batteries work with electrolytes in two circulations. Each circulation contains a redox system whose valence is changed during charging and discharging. The change in the valence of the two redox systems should take place at preferably high potential difference as this forms the equilibrium voltage of the battery. Figure 18.26 shows the principle of the redox-flow battery with the vanadium battery (equation (18.14)) as an example. The valence of all ions during each step can be seen in the figure.

Several different combinations of salts were and still are under investigation.

Fe-Cr $$\mathrm{Fe^{3+} + Cr^{2+} \rightleftarrows Fe^{2+} + Cr^{3+}} \qquad (18.12)$$

Br_2Cr $$\mathrm{Br_2 + 2Cr^{2+} \rightleftarrows 2Br^{-} + 2Cr^{3+}} \qquad (18.13)$$

Vanadium $$\mathrm{V^{5+} + V^{2+} \rightleftarrows V^{4+} + V^{3+}} \qquad (18.14)$$

Regenesys $$\mathrm{3NaBr + Na_2S_4 \rightleftarrows 2Na_2S_2 + NaBr_3} \qquad (18.15)$$

Several problems with redox-flow batteries have occurred and are still unsolved. The stability of the separator and the mixing of the electrolytes through the separators are severe problems. Therefore, the vanadium system became the centre of interest in the last few years as the materials and electrolytes are similar for the positive and the negative electrodes. Therefore, a crossing of ions through the separator just causes coulomb losses, but causes no deterioration of the electrolytes.

Defining the specific energy densities is difficult because of the independent sizing of the converter and the storage. Typical values for 20 kW/20 kWh vanadium redox-flow batteries are about 20 Wh/kg and 50 W/kg. For mobile applications in electrical cars, this is not enough, but for stationary, especially in load levelling, applications it is an interesting option. Figure 18.27 shows a prototype of a redox battery at laboratory scale