1 Introduction

The global energy supply will change in the years to come. “Renewable” energy sources are apparently an essential component to reduce carbon dioxide emissions and to achieve the goals established in the international Paris agreement [1,2]. Fortunately, they have become the most inexpensive energy source for electrical energy in the recent years [3]. Unfortunately, the provision of electrical energy from photovoltaics and wind power is not necessarily linked to the temporal demand for electrical energy. Three options are conceivable and probably a combination of all is essential to overcome this problem. The first option can be assigned to the generic term "smart grid", as one aspect of it deals with the shift in demand for electrical energy at times when it is available. However, this is only a possibility for some electrical consumers and processes, such as heat pumps to provide heat in buildings, charging battery-powered electric vehicles, operating certain domestic equipment (e.g. washing machines, freezer, battery powered devices), but becomes much more complex for industrial processes that rely on continuous production. The second option therefore utilizes the direct storage of electrical energy during an oversupply of solar and wind power in suitable systems that can feed the energy back into the grid at times of need. The conversion of electrical energy into specific compounds (i.e. hydrogen) that can be applied in other sectors, such as industry, mobility, heat or domestic applications are the third variant. Especially the second and third variant possess some interconnections, since for example hydrogen produced by water electrolysis during an oversupply of energy can be used for the production of heat, in fuel cell mobility, as raw material in the chemical industry (third option) or it can be converted back into electrical energy (corresponding to the second option). However, each conversion is correlated with a certain loss of energy, so the path of electricity to hydrogen and hydrogen back to electricity is not as efficient as the storage of electricity in pumped storage hydro power stations or the storage in batteries. Nevertheless, the decision for a single technology or for a whole national or global energy system always implies several issues, such as the energy storage duration (which is the time a fully charged system can release electrical energy at its nominal power), efficiency, power and capacity specific costs, cycle life, expected calendar life and reliability, thus no simple answer can be given.

Some reports have sketched future scenarios that predict the demand of several energy storage and energy conversion technologies for 2050 in Germany. The 85% scenario in a report of the Fraunhofer ISE represents an energy set-up where a reduction of 85% of carbon dioxide emissions related to the year 1990 is achieved [4]. To achieve this goal short duration stationary battery storage systems with a total capacity of 74 GWh, battery storage systems

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in electric vehicles connected to the grid with a total capacity of 81 GWh and pumped storage hydro power plants with a total capacity of 7 GWh are required for the direct storage of electrical energy from solar and wind power. Additional capacities are required for water electrolysis and methanation to produce energy carrying compounds that allow seasonal storage of energy.

In beginning of 2019 Tennet and Gasunie, a transmission system operator and a company that provides infrastructure and transportation for natural gas, presented an "Infrastructure Outlook 2050" based on a 95% carbon dioxide emission reduction target in 2050 for the Netherlands and Germany [5]. They stated that the share of different storage technologies was very sensitive to political requirements. When considering only the results for Germany, their "local" scenario with its main aim for energy independence, no import from neighboring countries and high amounts of decentral solar power (600 GW) resulted in a significant demand for battery storage (110 GW for Germany) and a high demand for water electrolysis (281 GW). The "national" scenario, aiming for energy independence, with strong supply of offshore wind power and limited energy exchange with neighboring countries corresponds to a comparable demand for water electrolysis (254 GW) but almost no need for battery energy storage (approx. 0 GW).

The most recent report published by Forschungszentrum Jülich comprises two scenarios with a 80% and 95% carbon dioxide emission reduction in 2050 related to the year 1990 [6]. They claimed no need for stationary battery energy storage since already 10% of the capacity of battery electric vehicles applied for grid purposes would be sufficient as short term energy storage. However, for the mid-term storage, their scenarios required compressed air-energy storage capacity of 24 GWh (with 400 MW nominal power, equivalent to 60 h discharge time) for the 80% target and 189 GWh (with 5 GW nominal power, equivalent to 38 h discharge time) for the 95% target. In both scenarios, long term energy storage capabilities are integrated via water electrolysis, methanation and storage of methane and hydrogen in already existing or newly installed methane storage caverns.

These three reports provide the clear message, that seasonal energy storage by water electrolysis with or without succeeding methanation is inevitable for a German economy with a low carbon dioxide footprint. The need for energy storage by stationary batteries, however, is somewhat more uncertain, as some scenarios predict a demand for them while others do not. Nevertheless, any battery technology that could provide short-term (a couple of hours) to mid-term (a few days) energy storage with competitive energy specific costs, efficiency and cycle-life will play an important role in the future energy storage market. The redox-flow battery is generally an energy storage system that can meet these requirements, but a multitude of redox-flow batteries with different electrolyte and electrode compositions have been designed and developed, each with its own characteristics. A brief introduction to redox-flow batteries and its different types can be found in the following section.

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1.1 Redox-flow batteries for stationary energy storage

A typical redox-flow battery comprises two vessels that contain dissolved redox-active compounds (mostly salts of metals in different oxidation states), at least one pump for each vessel that pumps the liquid through a stack of single redox-flow battery cells (c.f. Fig 1-1 A). One tank contains a dissolved redox-couple with a low redox potential (N_{red}/N_{ox}), thus defining its electrolyte as the negative electrolyte (NE), whereas the second tank holds the positive electrolyte (PE) with a more positive redox potential of its redox couple (P_{red}/P_{ox}). In each cell two electrodes are flown through by the electrolyte and during charging the oxidized species in the NE are reduced while the reduced species in the PE are oxidized, whereas the reaction is reversed in case of discharging the system. The overall reaction can be described simply as follows:

cell reaction: $$N_{red} + P_{ox}\ \text{(charged)} \leftrightarrows N_{ox} + P_{red}\ \text{(discharged)} \tag{1-1}$$

To prevent mixing of NE and PE both half cells are separated by a separator which can be a porous separator with sufficiently small pores or an ion exchange membrane, that prevents the transport of redox-active species, while still ionically conductive.

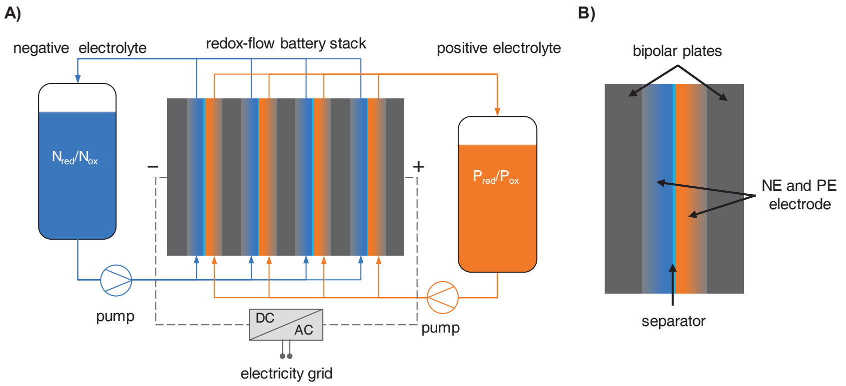

Figure 1-1: A) Schematic illustration of a redox-flow battery with two soluble redox active species in the positive electrolyte (PE) and negative electrolyte (NE), respectively. B) Main components of a single cell, such as bipolar plates separating two adjacent cells, two electrodes where the electrochemical reaction takes place and separator which prevents mixing of both electrolyte but maintains ionic conductivity.

This description of a redox-flow battery fits only to systems where both active species in the NE and PE are dissolved and where no active material is deposited as solid material in the electrodes (e.g. when N_{red} is a metal or when P_{ox} represents an insoluble metal oxide). Therefore, the amount of active species in the system is solely defined by the concentration and the volume of positive and negative electrolyte, while the nominal power is defined exclusively by the characteristics of the redox-flow battery stack (such as cell number, cell area, internal resistance of the cell). In principal, this enables a free scalability of power and

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energy capacity, which is often mentioned as the advantage of a redox-flow battery. However, even more important is the possibility to achieve low energy capacity specific costs for systems with a large energy capacity to power ratio, since only the costs of active species and additives in the electrolyte as well as costs for electrolyte tanks will dominate the costs of the whole system. Besides these systems with all soluble species, some redox-flow battery types exist, where at least one component is deposited as solid phase in the electrode while charging the system. Further variations exist, that replace one half-cell reaction of an ordinary redox-flow battery by a gas evolving or gas consuming reaction (hydrogen at the negative electrode or oxygen at the positive electrode) during charging and discharging. These systems that combine a solid or gaseous compound in one half cell to an ordinary liquid electrolyte in the other half-cell are classified as hybrid redox-flow batteries [7]. Typical examples of these class with solid compounds in the electrode are the zinc-bromine, the all iron, the all copper or the lead acid battery with soluble lead methanesulfonic acid [8–13]. Despite their use of more or less abundant and inexpensive active materials, the charging reaction in the negative half-cell leads to deposition of a solid metal phase at the electrode. This process always includes the risk of dendrite growth and short circuiting of the cell. In addition, the capacity of the cell is linked to the maximum amount of solid active material that can be stored within the cell, which affects the advantage of individual scalability of power and capacity.

Other hybrid redox-flow batteries make use of hydrogen at the negative electrode and thus they relate quite closely to hydrogen fuel cells. Instead of the slow oxygen reduction or oxygen evolution reaction the positive electrolyte is based on halide/halogen solutions or iron and vanadium salt solutions, that enable typically quite facile reaction kinetics and the storage of at least one charged compound in the liquid phase [7,14,15]. Especially the combination of hydrogen and iron(II)/iron(III) electrolyte could be an interesting option in an energy market that bases already on hydrogen due to its low cost, nontoxic electrolyte and the potential of cost savings, if a future hydrogen grid is used as hydrogen storage unit. Nevertheless, the platinum content that is required at the negative electrode to provide a sufficient catalytic activity could prevent the achievement of low cost targets, as well as the quite low cell voltages might limit its power density and efficiency.

All liquid redox-flow batteries

The class of all liquid redox-flow batteries comprises redox-flow batteries, where both half-cells are flown through by its own liquid electrolyte storing charged and discharged species as dissolved components within. This class contains the majority of different electrolyte chemistries, where several combinations of different positive and negative electrolyte chemistries are possible. Only some of them are depicted and presented here in brief.

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Iron-chromium redox-flow battery

The iron-chromium system is one of the earliest redox-flow battery technologies developed at the NASA Lewis Research center and uses a mixed electrolyte that contains dissolved iron and chromium salts in an acidic electrolyte. The electrolyte is applied in both half cells, although two separated electrolyte circuits are used, one for the positive and one for negative electrolyte. The Cr^{2+}/Cr^{3+} redox couple is active in the negative electrolyte while iron just remains as Fe^{2+}. In the positive electrolyte Fe^{2+}/Fe^{3+} is the active redox-couple and chromium remains inactive as Cr^{3+}. The system uses quite inexpensive compounds, and can be operated at high temperatures to approximately 65°C. The overall cell voltage is 1.19 V and the concentration of iron and chromium is approximately 1 M, thus achieving a theoretical energy density of 16 Wh/L. However, the negative half-cell reaction is slow and its redox-potential is quite low, thus hydrogen evolution as a side reaction is likely to occur, reduces the coulombic efficiency and requires a system design that can deal with charge imbalances between positive and negative electrolyte [7,16].

Titanium-manganese redox-flow battery

The titanium-manganese redox-flow battery was developed by Sumitomo Electric Industries and makes use of the relatively abundant elements titanium and manganese [17]. Titanium is varying between its oxidation states Ti^{3+} and TiO^{2+} and manganese between its oxidation states Mn^{2+} and Mn^{3+}, thus leading to a theoretical cell voltage of 1.41 V. However, the charged Mn^{3+} species tend to undergo disproportionation reaction and precipitate as MnO_2, which can lead to loss of capacity and potentially more severe damages by blocking the electrodes of the redox-flow battery. To mitigate this issue, the concentration of sulfuric acid and the concentration of titanium salts must be sufficiently high, while the concentration of manganese should not exceed 1 M. Such a setup yielded an energy density of 24 Wh L^{-1}, but the high redox-potential of the manganese redox couple leads to carbon corrosion. Since the MnO_2 precipitation still occurs at elevated states of charge leading to mass transport limitations and because the kinetics at least for the negative half-cell are too slow, further development is necessary to bring this type of redox-flow battery onto the market [18–20].

Quinone based organic redox-flow batteries

A first metal free redox-flow battery was presented by Huskinson et al., who applied 9,10-anthraquinone-2,7-disulfonic acid as the redox active component in the negative electrolyte and bromine in the positive electrolyte in an acidic aqueous electrolyte [21]. The quinone (and quinones in general) undergo a very rapid electron transfer reaction, enabling quite high power densities and its easy production from commodity chemicals anthraquinone and oleum offers the potential for low costs. However, the open circuit voltage in range of 0.7 to 0.9 V is quite low, and bromine/bromide as the positive redox couple comprises certain risks due to its toxicity, environmental hazards and high vapor pressure. To overcome this risk, Yang et al. dissolved 1,2 benzoquinone-3,5-disulfonic acid in diluted sulfuric acid to be used as the positive electrolyte [22]. As negative active component anthraquinone-2-sulfonic acid was applied, which is a similar approach to Huskinson et al. The experimental open circuit cell

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voltage decreased to values of roughly 0.5 V and the solubility of the organic components was quite low, hence they mentioned to introduce suitable functional groups into the quinone molecules to adapt solubility and cell potential. Accordingly, Lin et al. introduced more replaced sulfonic acid functional groups by hydroxy functional groups in the anthraquinone molecule, thus lowering its redox potential [23]. To maintain solubility, they used an alkaline electrolyte of 1 M potassium hydroxide solution, that even further decreased the pH dependent redox-potential of the anthraquinone redox couple. As positive electrolyte, they applied ferro/ferricyanide dissolved in 1 M potassium hydroxide. The cell voltage increased to 1.2 V and even higher voltages of up to 1.34 V were indicated by using anthraquinone with more hydroxy or methyl functional groups. Eventually, quinone based redox-flow batteries seem to offer some promising potentials for energy storage, but solubility and long term stability issues need to be addressed.

All-soluble all iron redox-flow battery

A redox-flow battery system that bases solely on the redox reaction of iron was published by Gong et al. who added triethanolamine to the negative electrolyte, which serves as organic-ligand to iron, lowering the redox potential of the Fe^{2+}/Fe^{3+} couple significantly. They used the ferro/ferricyanide couple in the positive electrolyte, while both electrolytes consisted basically of diluted sodium hydroxide solution (3 M). Their setup demonstrated a good performance at open circuit cell voltages of about 1.3 V and a quite stable discharge capacity over 110 cycles. Unfortunately, crossover of triethanolamine from the negative to the positive electrolyte across the membrane was identified as on major challenge as it increases the membrane resistance and can affect the properties of the positive electrolyte. Nevertheless, their work highlighted the possibility to adapt redox-potentials of redox couples by appropriate metal-organics ligands, which is not limited to iron.

All vanadium redox-flow battery

The most mature and most often used redox-flow battery was developed by Maria Skyllas-Kazacos in 1986 [24–26]. The aqueous electrolyte comprised of dissolved vanadium salts (concentration of 0.1 M) and 2 M sulfuric acid. The negative electrolyte contains V^{2+}/ V^{3+} species, while the positive electrolyte contains VO^{2+}/VO_2^+ species during charge and discharge. Although the first cell setup-was quite simple it still achieved coulombic efficiencies of more than 90% up to a state of charge of 70%, corresponding to a quite stable open circuit cell voltage of 1.3 V. In the following years, their group could show several improvements such as cell design, electrode pretreatment, electrolyte production and electrolyte stability [27–32]. One basic advantage of vanadium is its property to exist in four oxidation states, whereas two couples maintain a sufficient redox-potential difference and are soluble in aqueous electrolyte. Therefore, a vanadium redox-flow battery (VRFB), is unharmed by any cross contamination of vanadium from one side to the other, since this simply leads to a self-discharge reaction, but does not affect the system irreversibly. This property is quite exceptional among the elements of the periodic table and only a few distinctively more

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hazardous elements have comparable properties (Cr^{2+}/Cr^{3+} vs. Cr^{3+}/CrO_4^{2}, Np^{3+}/Np^{4+} vs. NpO_2^{+}/NpO_2^{2+})[7].

This list gives just a brief overview of some important redox-flow battery types. However, more combinations of different active species and electrolytes are already reported and the reader is referred to the literature for a more detailed overview. Just to name a few, other systems are semi-solid flow batteries [33], polymer-based organic redox-flow batteries [34], differential pH redox-flow batteries [35] and different aqueous and non-aqueous organic redox-flow batteries [36,37].

1.2 Vanadium redox-flow battery – basic properties

The vanadium redox-flow battery (VRFB) is the most mature redox-flow battery system and comprises several advantages compared to other redox-flow-batteries. In this thesis the VRFB is used as model system to develop new characterization and model validation methods for redox-flow batteries. Therefore, a brief description of its main components is presented.

Vanadium electrolyte

As already mentioned the electrolyte contains the four different vanadium species, dissolved in a sulfuric acid electrolyte. The typical vanadium concentration ranges from 1.5 M to 2 M vanadium whereas the total vanadium concentration lies about 4 M [32]. The temperature range is depending on state of charge as well as on vanadium and acid concentration. The upper temperature limit is restricted by the thermal stability of VO_2^{+}, since it tends to undergo an irreversible precipitation reaction building solid V_2O_5 particles. To prevent this precipitation the maximum temperature limit is often set to a value of about 40 °C, while higher concentrations of acid and lower SoC can increase this limit [38]. The lower temperature limit is attributed to the limited solubility of V^{2+} and V^{3+}, that start to crystallize at temperature lower than 15 °C, for a total sulfate concentration of 3 M and a vanadium concentration of 1.6 M [39]. Lower concentration of sulfuric acid increase the solubility and allow the decrease of the lower temperature limit. A mixed acid electrolyte using sulfuric and hydrochloric acid could widen the usable temperature window and increased the solubility of vanadium, but overcharging of the positive electrolyte would lead to chlorine gas evolution increasing the need for safety features to prevent overcharging and to handle potential evolution of chlorine gas [40].
The standard redox potentials of the main reactions in the positive and negative electrolyte (NE, PE) can be found in [41]. The main reactions in the NE and PE, as well as the overall cell reaction are as follows (discharge direction from left to right):

negative electrolyte: $V^{2+} \leftrightarrows V^{3+-} + e^{-}$ $E_{ref,NE} = -0.255$ V vs. SHE (1-2)

positive electrolyte: $VO^{2+} + H_2O \leftrightarrows VO_2^{+} + 2\,H^{+} + e^{-}$ $E_{ref,PE} = 1.004$ V vs. SHE (1-3)

overall cell reaction: $V^{2+} + VO_2^{+} + 2\,H^{+} \leftrightarrows V^{3+} + VO^{2+} + H_2O$ $E_{OCV} = 1.26$ V vs. SHE (1-4)

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The theoretical overall open circuit cell voltage E_{OCV} is 1.26 V, however practical cell voltages indicated higher values, that are probably related to activity effects and some sort of Donnan potential across the membrane [42]. The electrolytes conductivity at room temperature is higher for the PE ranging from about 290 to 410 mS cm^{-1} and the NE range is between 180 and 250 mS cm^{-1}, whereas both are depending on state of charge and temperature [43]. The electrolyte's viscosity lies in a range of about 4 to 6 mPas for room temperature condition and 1.6 M vanadium and about 4 M total sulfate concentration [44].

The main cost driver within the vanadium electrolyte is vanadium itself, since demineralized water is practically unlimited available and sulfuric acid is a commodity chemical. Vanadium is traded as ferrovanadium and as vanadium pentoxide, with only the pentoxide is used for electrolyte production due to its lower costs and its high vanadium amount without iron contamination. The price per kg vanadium pentoxide from 2000 to November 2019 is given in Fig. 1-2 and additionally the corresponding price per kWh of energy storage capacity is given. Since not the whole amount of vanadium can be utilized within a vanadium redox-flow battery, we assumed a vanadium utilization of 70% and a discharge voltage of 1.3 V (realistic only for high performance systems or low discharge current densities). The average value is around 12 € kg^{-1} vanadium pentoxide which equals capacity specific costs of about 91 € kWh^{-1}. The U.S. Department of Energy set a cost target of 150 \$ kWh^{-1} for energy storage technologies [45], hence for vanadium redox-flow batteries about two third of the cost target are already consumed by the high costs of the vanadium pentoxide. This indicates a certain need to optimize the whole system in terms of power density and resulting cost-reduction, as well as a need for quite high energy capacity to power ratios, since this lowers the effect of additional cost of cell stacks, pumps and the whole balance of plant.

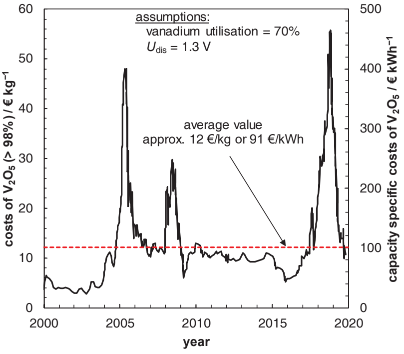

Fig. 1-2: Historical development of the costs for vanadium pentoxide and its corresponding costs for a kWh of energy storage capacity in a vanadium redox-flow battery system (cost of vanadium pentoxide based on [46] and exchange rate for USD to EUR taken from [47]).

The global mine-production of vanadium in 2018 was about $73 \cdot 10^3$ metric tons [48]. The biggest market share in 2018 had China with a value of 55%, followed by Russia (25%), South Africa (12%) and Brazil (9%). The global annual production corresponds to a theoretical

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maximum energy capacity of 24 GWh, which is just a third of the total required battery energy capacity for Germany in 2050 in scenario presented by Henning & Palzer [4]. When considering the global reserves and resources of vanadium, that are estimated to 20 million and more than 63 million metric tons [48] theoretical capacities of 6.6 TWh and 21 TWh are achievable. Although this would be theoretically more than sufficient for Germany's requirement of energy storage capacities, it is clear that this is an unrealistic approach and vanadium redox-flow batteries can be just one part amongst other energy storage systems in a future energy supply.

VRFB system components

A typical vanadium redox-flow battery system consists of two tanks, one for the NE and another one for the PE. Two pumps feed the electrolyte via appropriate pipes and hoses through the cell stack, where the charging and discharging reactions take place and the electrolyte then returns to the tank (c.f. Fig 1-3). The tanks are sealed and often purged with inert gases such as nitrogen or argon since the V^{2+} species undergo oxidation in contact with oxygen from air (or other sources), which needs to be prevented. Obviously, all components in contact to the electrolyte require corrosion resistant materials, due to the acidity of both electrolytes and their quite high and low redox-potentials.

The core component of the system is the cell, where the main reactions take place and which determines the main losses that are inevitable during charging and discharging. Losses in other system parts can be kept quite low, such as stray-current losses in the cell electrolyte inlet/ outlet hoses that lead to self-discharge, losses by providing pumping power, conversion losses in the AC-DC converter or losses in auxiliary equipment for battery management, safety-features and temperature control. The cell itself comprises basically four components: a bipolar plate that ensures separation between two adjacent cells, two electrodes typically porous carbon felt or carbon fiber electrodes and a separator.

The bipolar plate is typically the mechanical backbone of a single cell, that guarantees a sufficient mechanical stability. Additionally, it provides electrical contact between two adjacent cells, while preventing electrolyte contamination between these two cells. This can be achieved with compound materials based on mainly graphite and a low amount of polymer, such as polypropylene. For large cells or for cells that require low pressure drop the bipolar plate can include a flow field, which is a combination of several channels integrated into the bipolar plate that distribute the electrolyte across the cell.

The porous electrodes, which are often carried out as carbon felt electrodes must maintain a high surface area to reduce reaction overpotentials, while still ensuring a good electrical connection to the bipolar plate. Furthermore, the microscopic surface should provide a good wettability with the electrolyte and should facilitate the reaction by appropriate functional groups or defect sites on its surface. Nevertheless, the electrolyte must be pumped through the electrode, so a high permeability is necessary to limit the pressure drop across the cell inlet and outlet to an acceptable value.

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The separator provides ionic conductivity between both electrodes, while still separating both electrolytes, preventing cross-mixing and self-discharge of the cell. It can be executed as an anion exchange membrane, a cation exchange membrane or a microporous separator. Ion exchange membranes are usually hydraulically tight and allow only the selective migration of cations (mainly protons) or anions (sulfate anions) across the cation or anion exchange membrane, respectively. They cannot prevent the permeation of V^{2+} or V^{3+} from the NE side to the PE side or the permeation of VO^{2+} or VO_2^+ from the PE side to the NE side completely, hence this crossover leads to a certain self-discharge of the cell, that needs to be minimized. A microporous separator provides no specific selectivity and is permeable for the electrolyte. However, the permeability should be sufficiently low, so that any pressure fluctuations between negative and positive half-cell lead only to a minor electrolyte crossover. Small pores in the nanometer scale might have a beneficial effect on vanadium-crossover, since they could reduce the diffusivity of vanadium species within the pore, if they are just small enough.

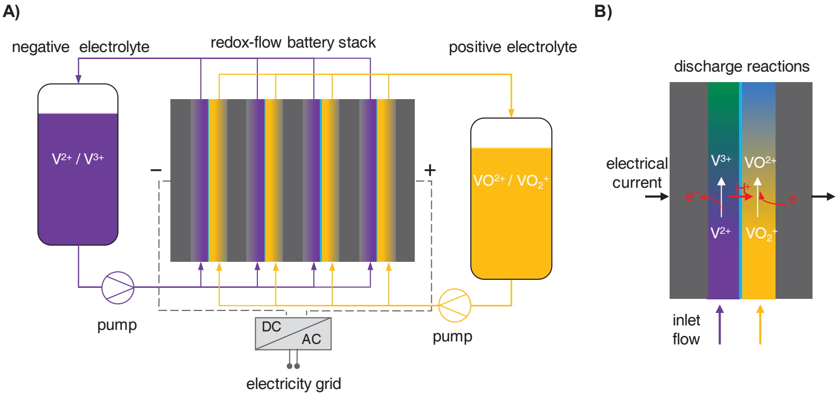

Figure 2-3: A) Schematic illustration of a vanadium redox-flow battery system and its components. B) Rough illustration of the reactions and electronic and ionic currents within a single cell of a vanadium redox-flow battery.

As already mentioned a low-cost design is mandatory to achieve the given cost target of the U.S. Department of Energy (150 \$ kWh^{-1} [45]). Since the costs for the vanadium electrolyte are presumably in a range of about 100 \$ kWh^{-1}, it is essential for the redox-flow battery stack to deliver as much power with as less investment as possible. This in turn, can be achieved whether by building a low-cost stack with moderate power densities, or by building a stack for moderate costs but achieving high power densities. Therefore, besides knowledge of the cost footprint of several components, an in-depth knowledge of the behavior of each component and its impact on power density, when modifying its key parameters is crucial. For this task modelling of redox-flow batteries is a helpful tool to understand the behavior of the redox-flow battery and to identify the limiting components that need improvement.

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