Understanding vanadium redox flow batteries

Battery technology | In the second of a two-part series for this journal, Jens Noack, Nataliya Roznyatovskaya, Chris Menictas and Maria Skyllas-Kazacos from CENELEST, a joint research venture between the Fraunhofer Institute for Chemical Technology and the University of New South Wales, examine the potential of vanadium redox flow batteries in the future energy system

With the increasing amount of renewable energies in an electrical grid, the need for compensation requirements increases in order to avoid shortfalls in coverage. Amongst the possible technologies available are electrochemical energy storage systems such as batteries, redox flow batteries (RFBs) and combinations of fuel cells and electrolysers [1]. RFBs differ from the other two technologies in that the energy is stored in liquid media and offer the possibility of charging and discharging in the same cell. This allows energy conversion and storage to be scaled separately and flexibly, adapted to the respective application, which in turn creates potential economic advantages over other technologies. Like all other electrochemical energy storage devices, RFBs can be realised in a wide range of size classes. Typical sizes range from a few hundred watts and watt hours of power and energy respectively, to systems with several megawatts and megawatt hours as large storage devices for grid tasks.

In principle, RFBs can be used for all stationary energy storage tasks, although storage times of several hours cause the lowest normalised energy storage costs [2,3]. To date, an almost unmanageable number of different types of RFB have been investigated [4,5]. However, the best-known representative is the vanadium redox flow battery (VRFB). VRFBs have potentially extremely high cycle lifetimes and are constructed with simple and inexpensive materials. This results in potentially low storage costs when used as safe and sustainable stationary energy storage devices in grids with renewable energy sources.

Compared to other storage technologies VRFBs have many advantages:

- High safety (non-flammable and no thermal runaway)
- Long service life and cycle life
- Separate scalability of power and energy
- Modular design
- No use of materials from politically unstable areas
- Easy recyclability

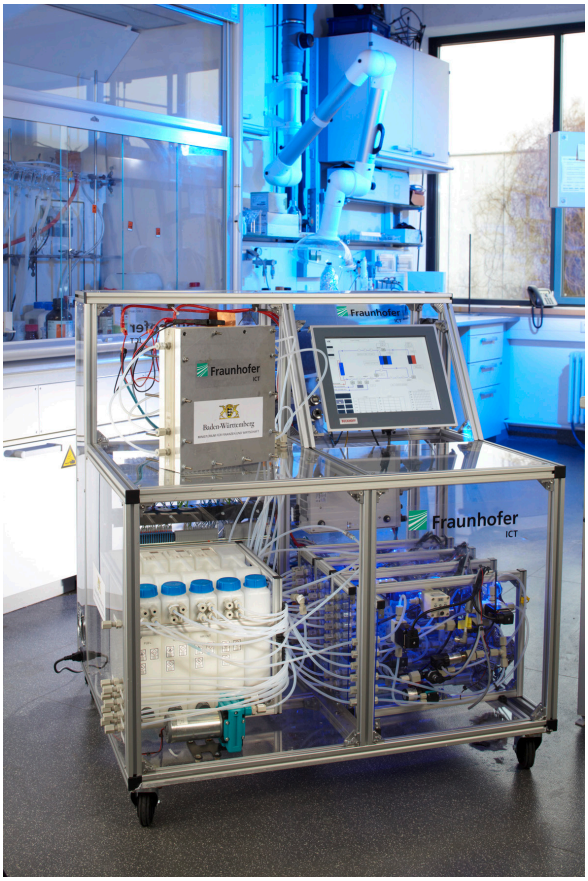

Figure 1. Kilowatt-class vanadium oxygen fuel cell system

Today's classical VRFB was developed in the 1980s at the University of New South Wales in Australia by Professor Maria Skyllas-Kazacos and her group and has been continuously improved until today [6]. Often several generations can be distinguished, whereby the energy density in particular, but also many other characteristics, differ from each other:

- Gen1: V/V-RFB (30 watt hours per litre)
- Gen2: V/Br-RFB (50-70 Wh/L)
- Gen3: V/V-RFB with mixed acids (~47 Wh/L)
- Gen4: V/O2- RFB or Vanadium/Oxygen fuel cell VOFC (~150 Wh/L)

Due to the relative simplicity of construction and operation, low cost and high safety, the VRFB (Gen1) is still the most studied and installed type of redox flow battery.

General principles of operation of VRFBs

The most important components of VRFBs are the energy converter, i.e. an electrochemical cell or cell stack formed from multiple cells, the energy storage medium (often referred to as the electrolyte), the fluidic system, the heat management and control system and the regulation technology for the interaction of all components. In the classical VRFB, the electrolyte consists of dissolved vanadium sulfates in sulfuric acid and a small amount of phosphoric acid that is used to increase the thermal stability of the charged positive half-cell electrolyte [7].

During operation, the two half-cell electrolytes are continuously pumped through the electrochemical cell, whereby the actual energy conversion reactions take place at the electrodes as oxidation and reduction reactions of the vanadium ions. The electrode is the phase boundary between the electronic and ionic conductor. At the positive electrode, tetravalent vanadium ions (V^{4+}) are oxidised to pentavalent vanadium ions (V^{5+}) during the charging process [8] [1]. During this process, an electron at the positive electrode is moved from a tetravalent vanadium ion via an electronic conductor to the negative

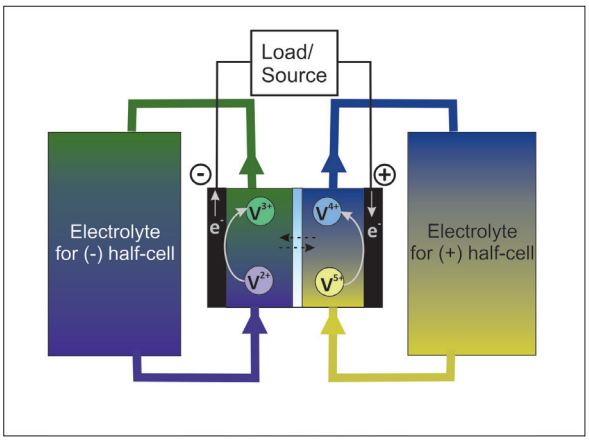

Figure 2. Schematics of vanadium redox flow batteries

electrode, using energy, and a trivalent vanadium ion (V^{3+}) is reduced by the electron to a divalent vanadium ion (V^{2+}):

Positive electrode:

$$V^{4+} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{5+} + e^-$$

$$\varphi^{0,+}_{VO_2^+/VO^{2+}} = +0.999\text{V}$$

Negative electrode:

$$V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+}$$

$$\varphi^{0,-} = -0.255\text{V}$$

Cell reaction:

$$V^{4+} + V^{3+} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{5+} + V^{2+}$$

$$U^0 = \Delta\varphi^0 = 1.254\text{V}$$

The discharging process is reversed accordingly under energy release. The achievable voltage of a cell is determined by the potentials (φ) of the reactions of the half cells of the positive and negative electrodes. Basically, the open circuit voltage of a cell is the difference between the positive and negative half-cell potentials plus a membrane potential:

$$U_{cell} = \varphi^+ - \varphi^- + \varphi_{membrane}$$

The potentials depend on various factors such as concentration (correlated with the state of charge – SOC), temperature, type of redox pair (standard potential) and, in the case of current flow, the speed of the reactions. The cell voltage during operation can be described in a simplified way as the open circuit voltage minus (discharging) or plus (charging) further voltage losses due to ohmic losses, speed of the reactions and mass transport losses:

$$U_{cell} = U_{OCV} \pm U_{losses}$$
$$= \varphi^+(c,T) - \varphi^-(c,T) + \varphi_{membrane}(c,T) \pm [IR_{ohmic}(T) + IR_{reaction}(c,T) + IR_{mass\ transfer}(c,T)]$$

All factors are at least dependent on the concentration of the substances involved in the reaction, resulting in the typical non-linear charge and discharge curves of batteries. For VRFBs, this means that the open circuit voltage of a fully charged cell is approximately 1.6 V and 0.8 V in the discharged state. The speed of the charging and discharging process depends directly on the current. However, there are always limits for batteries, which for various reasons must not be exceeded. With VRFBs, as with all batteries based on aqueous electrolytes, the charging voltage is limited by the electrochemical stability of water. Depending on the electrode material and the pH value, water decomposes into hydrogen and oxygen at certain potentials. At platinum electrodes (standard potentials) the difference between the potentials is 1.23 V. Apart from the costs, it would therefore not be possible to charge a VRFB with such electrodes even half full with a reasonable efficiency, since more and more hydrogen and oxygen would be produced during the charging process. Unfortunately, other metals have similar properties or even react, so that the electrodes of VRFBs are made of carbon-based materials. This increases the stability range of water, called the voltage window, to about 1.7-1.9 V and results in an upper voltage limit of approximately 1.65 V for VRFBs. Exceeding this limit, e.g. by excessive electric current, first leads to an intercalation of ions in the electrode material of the positive electrode and finally to the formation of highly reactive oxygen, which in turn reacts with the carbon electrode material to form carbon dioxide. Both effects lead to an irreversible increase of the internal resistance and thus to a loss of performance due to this ageing effect. At the negative electrode, however, an additional hydrogen formation takes place. As at the positive electrode, the speed of this side reaction depends exponentially on the magnitude of the voltage. At high charging rates, the voltage of a fully charged VRFB is very close to this limit, so the state of charge of commercial systems is usually limited to approximately 80% of the theoretical maximum capacity to reduce gassing side reactions and increase the lifetime of the VRFB. Higher states of charge can however be attained by utilising constant current – constant voltage charging profiles as used in other types of batteries.

As mentioned above, the VRFB requires some kind of membrane or separator to prevent the mixing of the two half-cell electrolytes [9,10]. If this would not be the case, V^{5+} would chemically react directly with V^{2+} to form V^{4+} and V^{3+}, releasing heat. The membrane provides a physical barrier to prevent mixing, but it must allow ions to migrate and complete the circuit. Since electrons migrate from one half cell to the other via the external circuit during charging and discharging, the resulting charge imbalances must be compen-

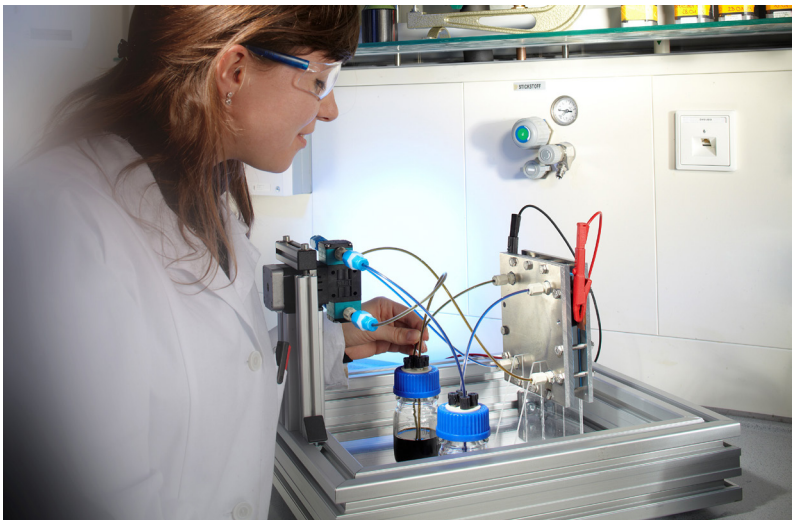

Figure 3. Vanadium redox flow laboratory test cell setup

<?> The tetra- and pentavalent vanadium ions are actually more complex compounds. Often they are given as vanadyl (VO^{2+}) or divanadyl cations (VO_2^+), but this again is a simplification of reality and the actual conditions are much more complex and the subject of research. For better comprehensibility V^{4+} and V^{5+} are used here.

sated for by ion migration through the separator to maintain electroneutrality. This balance is usually achieved by the migration of positively charged protons H^+ (actually hydronium ions - H_3O^+) in the acid electrolyte through the separator. The separator must have the highest possible conductivity for the balancing ions and a high barrier effect (high selectivity) for all other ions and molecules (water). The conduction of ions through the separator can become a speed-determining factor. In practice, however, it is usually a cost factor, since the separators used can be relatively expensive. In principle, all known types of separators can be used, including ion exchange membranes, microporous separators and solid ceramic ion conductors. For research purposes, mostly ion exchange membranes are used which have a high selectivity and relatively high costs. Microporous separators are porous polymer films which are much cheaper but have a low selectivity. Microporous separators are standard for lithium-ion batteries, but their use in the VRFB is complicated by the flowing and much lower viscosity electrolyte. Although coulombic efficiencies as high as 99% have been reported for VRFBs employing several types of ion exchange membranes, for other separators, the low viscosity leads to a higher diffusion of all substances, thus to a lower selectivity and to losses due to direct reaction of V^{5+} and V^{2+}, which results in higher efficiency losses as well as higher self-discharge.

Pressure differences of the flowing media can also lead to a direct transfer of electrolyte across the separator, causing further energy efficiency losses. Another important effect regarding the use of membranes and separators that must be considered is a continuous change in the volume of the two electrolyte solutions with cycle number. In the case of cation exchange membranes, the bulk electrolyte transfer is from negative to positive, while for anion exchange membranes, the net transfer is from positive to negative. This increases the volume of one electrolyte by reducing the other. There are several factors that affect this transfer, including osmotic pressure effects resulting from the different ionic strength of the two half-cell solutions. Another reason is that water molecules are transported across the membrane around the equalising hydrogen ions (hydrate shell) which is asymmetrical. If no countermeasures are taken, this effect will result in a continuous loss of capacity. In the case of the VRFBs

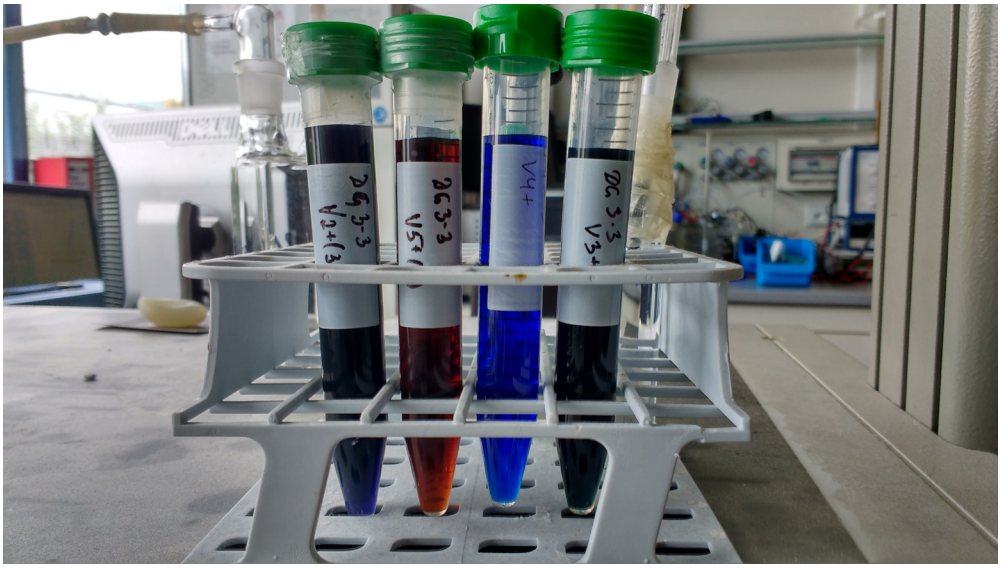

Figure 4. Vanadium electrolyte samples

however, this can readily be reversed by volume compensation. In practice, the volume of the two electrolytes is rebalanced by pumping electrolyte solution from one tank to the other by the battery management system (BMS) [11]. This is only possible because the same elements are used in both half-cells of the VRFB. This would not be possible if different elements were used.

Despite their poor performance to date, non-ionic separators continue to be investigated in an effort to reduce the costs of VRFBs. Suitable separators must be chemically stable, highly conductive to protons and with low permeability to the four vanadium ions. In parallel however, continuing cost reduction is being achieved in the production of highly stable ion exchange membranes. This is being made possible by the increased production volumes that are being achieved with the recent installation of MW-scale VRFB systems around the world.

Electrolyte raw material

Two electrolyte solutions are required for the operation of VRFBs: an acidic electrolyte solution containing the V(IV)/V(V) couple in the positive half cell and an acidic V(II)/V(III) electrolyte in the negative half cell. Both electrolytes are continuously pumped through their own half cells during charging and discharging. However, only a single electrolyte comprising a 50:50 mixture of V(III) and V(IV) is used as the starting solution in both half-cells, which in the classic VRFB contains a total vanadium concentration of approximately 1.6 M, 4 M total sulphate and additionally approximately 0.05 M phosphoric acid [12].

Vanadium oxide is used as a raw material and is dissolved in sulphuric acid supporting electrolyte to produce an equimolar amount of 0.8 M V^{3+} and 0.8 M V^{4+} as sulfate salts, although total vanadium concentrations up to 2 M are also used in special situations. The electrolyte solution containing the equimolar mixture of V^{3+} and V^{4+} is usually called $V^{3.5+}$ solution. An equal amount of this $V^{3.5+}$ electrolyte is used in both half cells at the beginning of the first charging process. In the first charging process, V^{3+} reacts first to V^{4+} on the positive electrode and V^{4+} to V^{3+} on the negative electrode. This produces a state of charge SOC=0 at a voltage of approx. 0.8 V. A second charging step converts V^{4+} to V^{5+} in the positive half-cell electrolyte and V^{3+} to V^{2+} in the negative. It is also important to note that due to the extremely slow reaction from V^{3+} to V^{4+}, a VRFB can only be electrically discharged up to a state of charge of SOC=0. Even a short circuit does not cause further discharge and a battery system would always be under high voltages, similar to lithium-ion batteries (maintenance problem). With VRFB, however, this problem can be bypassed simply

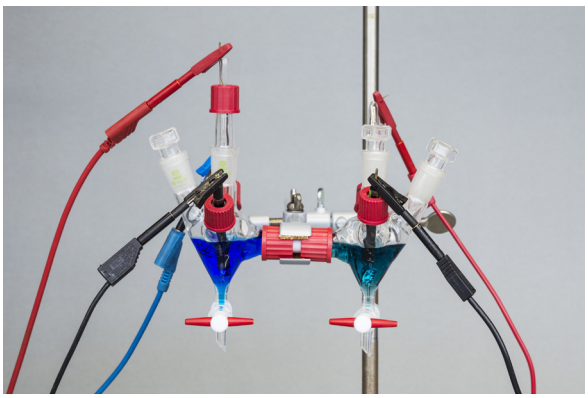

Figure 5. Discharged non-flow vanadium redox flow battery laboratory cell

by mixing both electrolyte solutions. The cell voltage drops quickly to 0 V and allows safe work on VRFB components.

Cells and stack

The electrochemical cell is the core component of a VRFB system. A cell has a voltage range of 0.8-1.6 V depending on the SOC as described above. To increase the voltage, multiple cells are connected electrically in series and hydraulically in parallel in a cell stack [14,15]. Typical voltages of stacks are approximately 24-70 V, although larger 100-cell stacks with much higher voltages have been produced. A high voltage is desirable due to lower power electronics costs, but the number of cells in a stack is limited by unwanted shunt currents.

The cells of VRFBs are symmetrically designed and consist of two half cells separated by a separator. Due to the similar reactions, the same materials can be used in both half cells. There are two fundamentally different cell design concepts: porous felt electrode based half cells and cells with structured bipolar plates [16]. The typical design is based on felt electrodes. Cells with structured bipolar plates are much more complex and can be designed as flow-by or flow-through design, as in fuel cells. Cells with structured bipolar plates incorporate very thin carbon paper electrode materials and a so-called "zero-gap' configuration that allows significantly higher power densities, but may have higher costs. In the classic felt-based flow-through design, both electrolytes flow through carbon-based graphite felts several millimeters (typically 2-4 mm) thick, which serve as the electrodes. The graphite felt is embedded in a flow-through frame which in turn distributes the electrolyte within the cell and stack. Graphite-based plates (bipolar plates) are used to hydraulically seal the individual cells tightly while simultaneously providing electrical conductivity between adjacent cells. Typical operating current densities of a cell cover a wide range and can reach average values between 50-150 mA/cm^2, although the maximum current can be considerably higher in the case of high-power density cell designs. A stack with an electrode area of 1,000 cm^2 per half cell and 25 cells can thus achieve a power output of between 1.25-3.75 kW at an average cell voltage of 1.0 V during discharge in conventional cell designs. Power densities of 5 kW/m^2 have however been reported for high power density cell designs [14].

Figure 6. Control room of a 2 MW/20 MWh vanadium redox flow battery at Fraunofer ICT

System

The special features of VRFBs require a process technology similar to that of fuel cells for safe and long-term operation, but much less complex. In a VRFB system at least one or more stacks are first electrically connected in parallel and/or serially to achieve the voltage and current values required for the power electronics. As with the stacks themselves, however, there are voltage limits due to shunt currents [17]. The shunt currents are also created here by the parallel hydraulic paths through the individual stacks fed from common electrolyte tanks. In practice, the influence of shunt currents can be minimised simply by using multiple tanks and pumps and as many inverters as possible. Ideally, each individual stack should have its own tanks and inverter, but this may not be cost effective.

The amount of electrolyte solution determines the amount of energy in the battery. One litre of a 1.6 M vanadium electrolyte solution has a theoretical maximum capacity of 21.6 Ah. At an open circuit voltage of 1.4 V, this results in a maximum energy content of 30 Wh/L. It should be noted, however, that this quantity corresponds to 0.5 L electrolyte for both negative and positive half cell. In reality, the dischargeable energy content is lower due to the factors mentioned previously. These include, in particular, the current density dependent efficiency of the discharge process, the temperature and the limitation of the charge state range.

Figure 7. Two kilowatt-class vanadium redox flow battery test systems

The two electrolytes are stored in tanks and are pumped in parallel through each individual cell of the system. The energy loss due to pumping the electrolyte is about 5% and can be optimised by modularisation. This can be achieved by building the entire system with a number of identical modules and using different numbers depending on the power requirements. Another possibility is the sole modularisation of pumps to operate the pumps at maximum efficiency at partial load. A further necessity is the regulation of the volume flow with the change of current and state of charge. During discharge at high SOC the flow rate requirement is lowest and increases exponentially with decreasing SOC due to decreasing concentration of the active species in solution and the mass transport requirements at the electrode. Considerable work is currently being carried out on intelligent flow controllers that continually adjust the flow rate to minimise the parasitic pumping energy losses and maximum overall energy efficiencies of flow batteries.

Due to the corrosive nature of the acidic V(V) electrolyte in the positive half-cell and possible side reactions, all parts of a VRFB system in contact with the medium must be designed free of metal. For this reason, polymers such as polypropylene (PP) or polyvinyl chloride (PVC) are used as materials for cell frames, pipelines, tanks and all other parts in contact with the medium. The two electrolytes must be protected against oxidation by atmospheric oxygen. V^{2+} ions in particular react strongly with the oxygen in the air, resulting in a loss of capacity. The negative electrolyte tank is usually sealed from the atmosphere and is often de-oxigenated and covered with protective nitrogen gas layer over the electrolytes in the tanks. The use of a protective layer comprising an inert oil such as paraffin has also been proposed as a blanket to prevent air oxidation in the negative half-cell electrolyte tank.

Air oxidation is one process that leads to an imbalance in the half-cell SOCs that causes capacity loss, so this needs to be avoided. There are processes that allow electrolytes oxidised by atmospheric oxygen to be regenerated and thus restore the original capacity however. For example, the reaction can be reversed electrochemically using electric current and oxygen is released again [18]. Chemical regeneration can also be used to restore capacity losses caused by these side reactions.

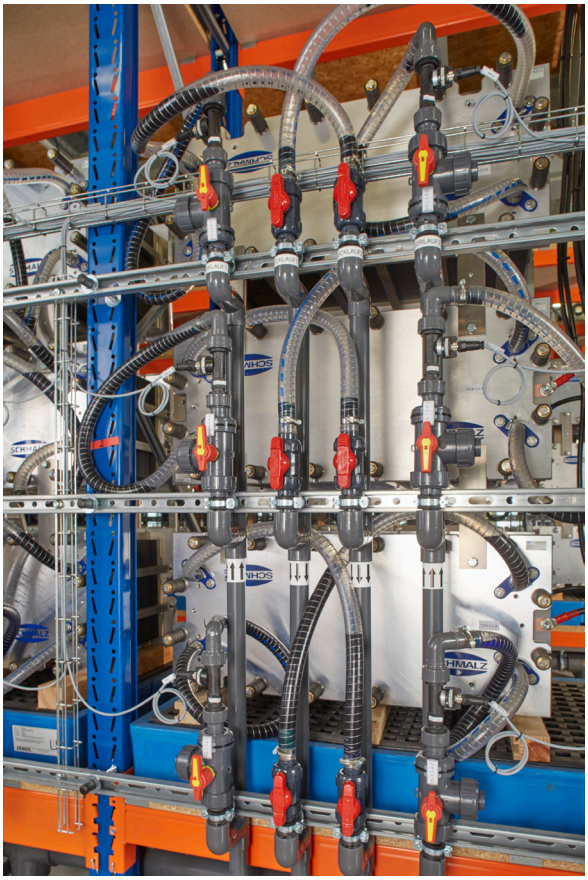

Figure 8. Piping and stacks of a 2 MW/20 MWh vanadium redox flow battery at Fraunhofer ICT

As with all large-scale processes a good battery management system also requires a certain number of sensors and actuators for efficient monitoring and operation. These include flow and pressure sensors, temperature sensors and an open circuit voltage sensor. The open circuit voltage sensor is a special feature for RFB systems (not for hybrid systems!) that allows the SOC to be determined at any time and especially with current flow. The open circuit voltage sensor is often a separate single and smaller cell as used in stacks. The flow sensors are necessary for the regulation of the pumps and thus for the increase of the efficiency of the VRFB system. Pressure sensors can be installed for safety reasons to detect possible pressure overruns. However, passive fuses can also be installed as a form of pressure relief.

The temperature sensors are necessary to detect temperature minima and maxima and where necessary to perform active thermal management. The vanadium solution used in VRFBs is highly concentrated to achieve the highest possible energy content and the vanadium salts are at the limit of solubility at the supplier specified maximum and minimum operating temperatures. The thermal stability of V^{5+} determines the upper temperature limit of VRFBs by a reaction which leads to an irreversible precipitation of solid vanadium oxide depending on V^{5+} concentration, temperature and time. For this reason, the maximum temperature in the electrolyte is limited to 40°C for a 1.6 M vanadium electrolyte. Thus, only a range at high states of charge at high temperatures becomes critical, which is why the storage of partially discharged or discharged batteries at high ambient temperatures is no problem. Normally the heat generated from the electrolyte is dissipated by electrolyte-air heat exchangers.

Safety

VRFBs are a relatively safe technology. Due to the use of aqueous electrolytes, the fire risk of VRFB systems is much lower than with other technologies. Overcharging the battery does not lead to fire but to a reduction in battery performance and ageing of the stacks. Thermal runaway as with lithium-ion batteries is excluded. Precisely because of ageing, the voltage is continuously monitored as with all other battery systems. A deep discharge is possible, and this even increases safety by the resulting cell voltage of 0 V.

In addition to its corrosive character, vanadium electrolyte solution is classified as toxic and hazardous to ground water. However, it should be noted that the electrolyte is used in a closed system and vanadium can escape solely through electrolyte leaks. For this reason, VRFBs have a secondary containment to prevent the escape of vanadium solution into the environment.

In spite of the measures described above, there will always be a small amount of hydrogen produced during charging at high states of charge, which is a safety risk due to the possible explosive reaction with atmospheric oxygen. The amount is extremely small, but must be taken into account when installing the battery. For this purpose, the gas is discharged from the negative tank into the environment through a simple pipe and the battery room or container is well ventilated and flushed with fresh air to prevent any build-up of hydrogen gas.

Recycling

Unlike other compact battery types such as lithium-ion batteries, VRFBs are relatively easy to recycle by common methods. The battery system components can be

divided into electronics, fluid technology, stacks and electrolyte, with the last two components being the only ones that require analysis. Stacks ultimately consist solely of steel, copper, plastics and carbon. Stacks can be disassembled into their individual components and almost all components can be returned to the material cycle. For membranes and gaskets as well as carbon-based materials such as electrodes and bipolar plates, thermal recycling is necessary, but is energetically positive. Recycling of electrolyte can take place in two ways: as starting material for metallurgy or as recycled electrolyte for VRFBs. Used vanadium electrolyte ultimately represents a highly concentrated source of vanadium. The vanadium price has a low of approximately US$10/kg today at the beginning of 2020. Nevertheless, because of the high concentration, the material value of the electrolyte is still high after the battery has reached the end of its life. As with lead-acid batteries, the material value of vanadium can be taken into account in the running costs. Leasing models for vanadium electrolyte already exist.

Costs

In general, the comparison of battery systems should not be based on investment costs, but rather on the energy-specific lifetime costs for the respective application (levelised cost of storage – LCOS). LCOS takes into account the physical and economic characteristics of battery systems, which makes clear differences between different technologies. Even better, however, is the consideration of the levelised cost of energy (LCOE) for the entire energy grid in which the battery is to be integrated. Depending on the application and the amount of renewable sources, the entire grid must be adapted to the requirements of the consumers and the potential for generation. Therefore, simulation programs must be used for the design in order to achieve the lowest possible LCOE. This leads, for example, to such constellations in which a grid with a low-efficiency energy storage system achieves lower LCOE than a battery with a high efficiency. The cost of efficiency losses can be compensated by a higher share of low-cost PV generation if the storage system also offers other advantages. Turnkey VRFBs today have an investment cost of less than US$700/kWh for a 20-year life.

Summary

VRFBs have progressed beyond the prototype and demonstration stage in recent years. Due to the extremely high vanadium price in 2018, commercialisation efforts of VRFBs were severely curbed but are currently experiencing a renewed upswing. Today, more and more systems in the megawatt hour range are being installed worldwide, as are smaller container-based VRFBs. The largest system with 200 MW and 800 MWh is currently under construction in China. In Australia, several plants with a total of over 200 MWh are being planned. Alongside lithium-ion batteries, they are now one of the most important stationary energy storage technologies, especially for grids with renewable energies and with average storage times of a few hours. The costs for VRFBs have fallen significantly in recent years and a further reduction in costs with a simultaneous increase in service life can be expected in the next few years as alternative production technologies are used and economies of scale gain influence. ■

Authors

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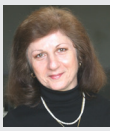

Maria Skyllas-Kazacos AM is an emeritus professor in chemical engineering at UNSW Sydney Australia. She is one of the original inventors of the all-vanadium redox flow battery and holds more than 30 patents relating to the technology. She is a fellow of the Australian Academy of Technological Sciences and Engineering and has received several awards including Member of the Order of Australia, the CHEMECA Medal and the Castner Medal.

References

[1] Dunn, B.; Kamath, H.; Tarascon, J.-M. Electrical Energy Storage for the Grid: A Battery of Choices. *Science* **2011**, *334*, 928-935, doi:10.1126/science.1212741.

[2] Viswanathan, V.; Crawford, A.; Stephenson, D.; Kim, S.; Wang, W.; Li, B.; Coffey, G.; Thomsen, E.; Graff, G.; Balducci, P.; et al. Cost and performance model for redox flow batteries. *Journal of Power Sources* **2014**, *247*, 1040-1051, doi:10.1016/j.jpowsour.2012.12.023.

[3] Noack, J.; Wietschel, L.; Roznyatovskaya, N.; Pinkwart, K.; Tübke, J. Techno-Economic Modeling and Analysis of Redox Flow Battery Systems. *Energies* **2016**, *9*, 627, doi:10.3390/en9080627.

[4] Noack, J.; Roznyatovskaya, N.; Herr, T.; Fischer, P. The Chemistry of Redox-Flow Batteries. *Angew. Chem. Int. Ed.* **2015**, *54*, 9776-9809, doi:10.1002/anie.201410823.

[5] Winsberg, J.; Hagemann, T.; Janoschka, T.; Hager, M.D.; Schubert, U.S. Redox-Flow Batteries: From Metals to Organic Redox-Active Materials. *Angew. Chem. Int. Ed Engl.* **2017**, *56*, 686-711, doi:10.1002/anie.201604925.

[6] Parasuraman, A.; Lim, T.M.; Menictas, C.; Skyllas-Kazacos, M. Review of material research and development for vanadium redox flow battery applications. *Electrochimica Acta* **2013**, *101*, 27-40, doi:10.1016/j.electacta.2012.09.067.

[7] Choi, C.; Kim, S.; Kim, R.; Choi, Y.; Kim, S.; Jung, H.-y.; Yang, J.H.; Kim, H.-T. A review of vanadium electrolytes for vanadium redox flow batteries. *Renewable and Sustainable Energy Reviews* **2017**, *69*, 263-274, doi:10.1016/j.rser.2016.11.188.

[8] The tetra- and pentavalent vanadium ions are actually more complex compounds. Often they are given as vanadyl (VO^{2+}) or divanadyl cations (VO_2^+), but this again is a simplification of reality and the actual conditions are much more complex and the subject of research. For better comprehensibility V^{4+} and V^{5+} are used here.

[9] Gubler, L. Membranes and separators for redox flow batteries. *Current Opinion in Electrochemistry* **2019**, *18*, 31-36, doi:10.1016/j.coelec.2019.08.007.

[10] Prifti, H.; Parasuraman, A.; Winardi, S.; Lim, T.M.; Skyllas-Kazacos, M. Membranes for redox flow battery applications. *Membranes (Basel)* **2012**, *2*, 275-306, doi:10.3390/membranes2020275.

[11] Yuan, X.-Z.; Song, C.; Platt, A.; Zhao, N.; Wang, H.; Li, H.; Fatih, K.; Jang, D. A review of all-vanadium redox flow battery durability: Degradation mechanisms and mitigation strategies. *International Journal of Energy Research* **2019**, *50*, 88, doi:10.1002/er.4607.

[12] Skyllas-Kazacos, M.; Cao, L.; Kazacos, M.; Kausar, N.; Mousa, A. Vanadium Electrolyte Studies for the Vanadium Redox Battery-A Review. *ChemSusChem* **2016**, *9*, 1521-1543, doi:10.1002/cssc.201600102.

[13] USGS National Minerals Information Center. Vanadium 2018 **2019**.

[14] Skyllas-Kazacos, M.; Kasherman, D.; Hong, D.R.; Kazacos, M. Characteristics and performance of 1 kW UNSW vanadium redox battery. *Journal of Power Sources* **1991**, *35*, 399-404, doi:10.1016/0378-7753(91)80058-6.

[15] Ping Zhao, Huamin Zhang, Hantao Zhou, Jian Chen, Sujun Gao, Baolian Yi. Characteristics and performance of 10 kW class all-vanadium redox-flow battery stack. *Journal of Power Sources, 162, 1416-1420* **2006**.

[16] Aaron, D.S.; Liu, Q.; Tang, Z.; Grim, G.M.; Papandrew, A.B.; Turhan, A.; Zawodzinski, T.A.; Mench, M.M. Dramatic performance gains in vanadium redox flow batteries through modified cell architecture. *Journal of Power Sources* **2012**, *206*, 450-453, doi:10.1016/j.jpowsour.2011.12.026.

[17] Tang, A.; Bao, J.; Skyllas-Kazacos, M. Studies on pressure losses andw flow rate optimization in vanadium redox flow battery. *Journal of Power Sources* **2014**, *248*, 154-162, doi:10.1016/j.jpowsour.2013.09.071.

[18] Noack, J.; Roznyatovskaya, N.; Pinkwart, K.; Tübke, J. Vanadium proton exchange membrane water electrolyser. *Journal of Power Sources* **2017**, *349*, 144-151, doi:10.1016/j.jpowsour.2017.03.039.