All-vanadium aqueous rechargeable lithium-ion batteries: The green macro-battery

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The lead-acid battery, which was invented in 1859 by French physicist Gaston Planté, is the oldest type of rechargeable battery. These batteries are used in a variety of applications, such as motor vehicles, boats and standby power installations. Since the technology is 155 years old, there is a need for exploring alternatives. Aside from the global movement towards greener technology, the search for new technology is driven by the need for a safer rechargeable battery. The lead in lead-acid batteries can cause lead poisoning and the battery's sulphuric acid is highly corrosive.

South Africa has abundant wind and solar energy sources, and yet the country mainly relies on coal as a power source. Renewable energy sources are cyclical. A cost-effective energy storage technology is required if these power sources are to ever significantly contribute to the country's energy needs. Due to its lower cost, the lead-acid battery is still the most widely used battery for large-scale energy storage. It is environmentally unfriendly, however, and has poor deep discharge and long-term cycling performance. The all-vanadium aqueous lithium-ion battery (VARLB) is a better alternative.

The research path leading to the VARLB started with investigations around increasing the energy density of the regular vanadium redox battery (VRB). Due to its long life span, the VRB is a promising energy storage technology for the large-scale energy storage market. The VRB is a redox flow cell.

Redox flow cells differ from commercial voltaic cells in the sense that energy is stored in charged electrolytes, not in the cell's electrodes. The reactants and products all remain dissolved throughout the charge and discharge cycle. An ion-selective membrane is required to keep the solutions from mixing. The cell short-circuits if the solutions mix, which forms heat. In the VRB, vanadium-based half-cell reactions are used in both electrodes. This eliminates the common flow cell problem of cross-contamination. The mixing of the electrolytes inevitably occurs due to the membranes leaking slightly. In VRBs, only vanadium compounds are formed when mixing occurs. These reactions can easily be reversed by recharging the cell. Therefore, the electrolyte theoretically has an infinite life span.

Unfortunately, the high cost of the VRB has hampered its commercial application. The main cost factors are the inherent low energy density and the necessity of using an ion-selective membrane. The energy density is limited by the solubility of the vanadium compounds, which are used as active materials. Water typically comprises more than half of the weight of typical electrolytes (Rychcik and Skyllas-Kazacos, 1988). The ion-selective membrane separator comprises approximately 20% of the battery cost (Prifti et al., 2012). Eliminating the water and the membrane therefore holds the key to high energy and cost-effectiveness.

Surface-supported active material tests

Initial experiments with ion exchange substrates and super capacitor substrates were conducted. The idea was to support the active ions of the VRB on a solid surface, rather than dissolving them. This immediately removed the energy density limit placed by the solubility of the active substances. This also makes an ion-selective membrane separator redundant, because the active materials are immobilised on the electrode surfaces. These initial trials led to a battery that uses the lithium-ion battery storage mechanism.

Lithium-ion batteries

Lithium-ion batteries have the highest energy density and longest life span of all the commercially available battery technologies. Organic electrolytes have classically been used to maximise the usable voltage window, and therefore the energy density of the battery. Organic electrolytes are required due to the extreme reactivity of lithium with moisture and air, but they are toxic, flammable and expensive. The production costs of traditional lithium-ion batteries are inhibiting for the large batteries required for load levelling (Wessels et al., 2012).

The costs are high because of the use of expensive organic electrolytes, safety concerns with large-scale batteries and because moisture- and air-free controlled environments are required for manufacturing.

Aqueous rechargeable lithium-ion batteries

Aqueous rechargeable lithium-ion batteries (ARLBs) are less dangerous replacements for standard lithium-ion batteries and are inexpensive. The stable voltage window of aqueous electrolytes (without considering electrode overpotentials) is 1.23 V, compared to the normal hydrogen electrode (NHE), and approximately 3 V for organic electrolytes. Figure 1 pairs the stability range of water with the reaction potential of a few materials that have been tested in lithium-ion batteries. Combining a suitable half-cell pair in the stability range of water creates an ARLB.

The left side of Figure 1 shows the O_2/H_2 evolution potential versus the normal hydrogen electrode (NHE) for a different pH in 1 M Li_2SO_4 aqueous solution. The right side shows the lithium-ion intercalation potential of various electrode materials versus NHE and Li/Li^+. AC: activated carbon, NASICON: materials with NASICON structure (Luo et al., 2010).

Aqueous electrolytes generally have ion conductivities of approximately two orders of magnitude higher than those of organic electrolytes, and are non-toxic and non-flammable (Luo et al., 2010). The fabrication costs are much lower for ARLBs, because no environmental control is required during manufacturing to limit air and moisture levels. This makes the ARLB ideally suited for the large-scale energy storage market, which requires batteries with a low cost, high safety characteristics and a long life.

All-vanadium oxide ARLB

The all-vanadium oxide ARLB is a special ARLB. It is based solely on vanadium compounds, just like the VRB. A symmetrical vanadium oxide ARLB combines the strengths of the regular VRB and other non-symmetrical ARLBs. This battery requires no ion-selective membrane and has an inherently high energy density, because the solubility of the reactants does not limit the energy density. Cross-contamination of soluble vanadium compounds should not cause any irreversible side reactions. Despite the wide interest in the VRB and the extensive studies on lithium-ion intercalation compounds, no publications could be found on an ARLB based solely on vanadium compounds.

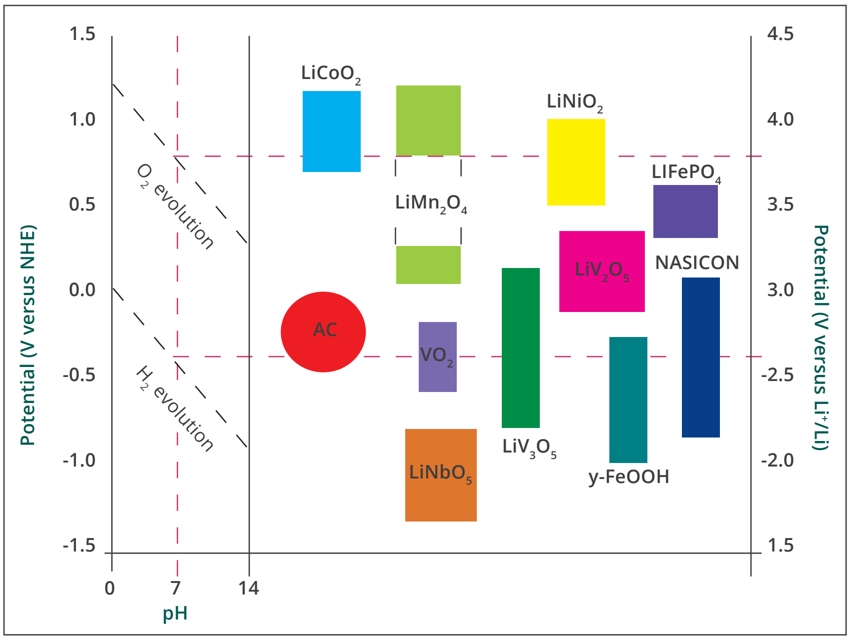

Figure 1: The half-cell reduction potential map of some lithium-ion battery materials.

Combining VO_2 and LiV_2O_5 (Figure 1), the expected cell reactions are as follows:

Cathode (reduction):

$V_2O_5 + e^- + Li^+ \rightleftharpoons LiV_2O_5$ .... $E_0 = 0.33$ V

Anode (oxidation):

$2Li_{0.5}VO_2 \rightleftharpoons 2VO_2 + e^- + Li^+$ .... $E_0 = -0.42$ V

Cell:

$V_2O_5 + 2Li_{0.5}VO_2 \rightleftharpoons LiV_2O_5 + 2VO_2$....... $E_0 = 0.75$ V

The expected specific capacity of a symmetrical vanadium oxide ARLB is in the range of 120 mAhg-1. The specific energy density using a cell voltage of 0.75 V is therefore 90 Whkg-1, which is almost double that of the lead-acid battery.

Ongoing research

So far, tested experimental cells have reached about a third of the expected theoretical energy density. Cell resistance is still a problem, but the optimisation of the electrode formulation and manufacturing process is underway to improve this. The use of graphene foam as current collector is an exciting prospect, and this super-conductive material may solve the cell resistance problem. A research team led by Prof Ncholu Manyala, an associate professor in the Department of Physics at the University of Pretoria, is the world leader in graphene foam produced by chemical vapour deposition, and will collaborate on the VARLB project.

References

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