A Southern African perspective of battery materials

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Recent developments in energy storage and the development and application of the ZEBRA, redox flow and lithium ion batteries and supercapacitors are reviewed. Opportunities for Southern Africa in research and as a supplier of high purity metals used in advanced energy storage systems are discussed

INTRODUCTION

Batteries are devices that store and deliver energy on demand by converting chemical energy into electrical energy. Chemical reactions suitable for this purpose may be split into respective electron donating and accepting half cell reactions, and locating these on electrically conducting electrodes separated by an electrolyte. The electrolyte conducts charge through ion flow only, thus forcing the commensurate flow of charge by electron conduction through the external electrical circuit allowing external charging and extraction of energy to and from the device. Conventionally only devices that stored both reagents and products within the device were called batteries but the trend is to now include devices that store electrical energy not only in the form of discernible half cell reactions as in the lead-acid battery (LAB), but also in the form of intercalated species such as in lithium ion batteries (LIB), or in the form of near surface charge movement or exchange as in supercapacitors (SC), or with the external store of reagents and products as in redox flow batteries (RFB) or fuel cells (FC).

The need to decarbonise transport and buffer intermittently produced renewable energy stimulated the development of more efficient and cheaper energy storage devices. Automotive propulsion requirements are very demanding, requiring both high power and energy densities as well as affordability. Stationary energy requirements are less demanding and were in the past mostly met using pumped water storage and LAB (Gür, 2018). New generation batteries will also become more attractive for this purpose as second life use of high performance mobile batteries will offer strong competition to stationary-only devices such as flow batteries, mechanical and pumped storage devices. Some idea of the applicability of the different devices and batteries in terms of power and energy requirements is given in Figure 1. Peak demands may best be met by a combination of devices such as a supercapacitor to provide power bursts and allow fast charging for lower power and energy intensive lithium ion batteries, flow batteries and pumped storage.

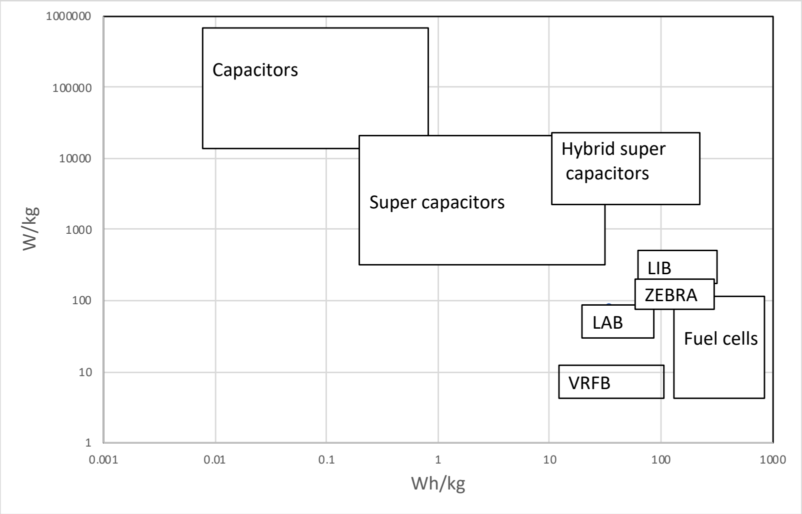

Figure 1. Relative power and energy capabilities of electrical energy storage devices. Data from Gür (2018), Sahin et al. (2022) and Dustmann (2004).

The feasibility of transitioning transport to clean energy hinges on the clean and affordable production of energy-intensive, highly reversible and durable storage devices. This must of course all be achieved cheaply with readily available and environmentally acceptable and recyclable materials. It is thus indeed no surprise that very few of the many possible battery systems have achieved significant market acceptance as reflected in almost equal market segments held by alkaline Leclanché, lead acid and lithium ion cells in 2020, with the latter the only recently developed group of devices and the only one showing significant growth (Zhao *et al.*, 2021). There are many types of batteries in niche applications but in the present context only the markets for metals used in LIB systems are expected to be significantly affected, i.e. between 2018 and 2030 the market for lithium is expected to increase by 6.4 times, for high purity nickel by 24 times, cobalt by 2.1 times and manganese by 1.2 times (World Economic Forum, 2019).

Lithium ion batteries presently dominate and will probably continue to do so for the immediate future as well as dominate high performance mobility applications. However, with chemistries changing in response to fluctuating metal prices, new technologies and market conditions, technology changes can be expected. Of note are major research programmes aimed at developing alternative systems such as sodium-based ion batteries (SIB), lithium metal batteries and combined technologies using supercapacitors that would allow higher power inputs and extractions. These and systems of importance in the South African context such as the ZEBRA sodium-nickel chloride high temperature battery, the all-vanadium flow battery (VFB), LIB and supercapacitors will be discussed in the context of prospects and possible impact on metal demand.

ZEBRA (ZEolite Battery Research Africa or Zero Emission Battery Research Activity)

The oil crisis in 1973 stimulated research into energy conversion and storage devices for renewable energy buffering and transport applications. The advantages offered by ion conducting solid electrolytes created the possibility of using liquid electrodes such as in the sodium-sulfur battery operating above the melting points of sodium and sulfur with molten electrodes, these separated by an ion conducting solid electrolyte such as β′′-alumina. In a joint South African and British research effort, a similar battery, but with a nickel/nickel chloride positive, was developed as the so-called ZEBRA battery (Van Zyl, 1996; Sudworth, 2001). The cell reaction indicated in equation 1, delivers a cell potential of ~2.6 V, with the cell configuration shown in Figure 2.

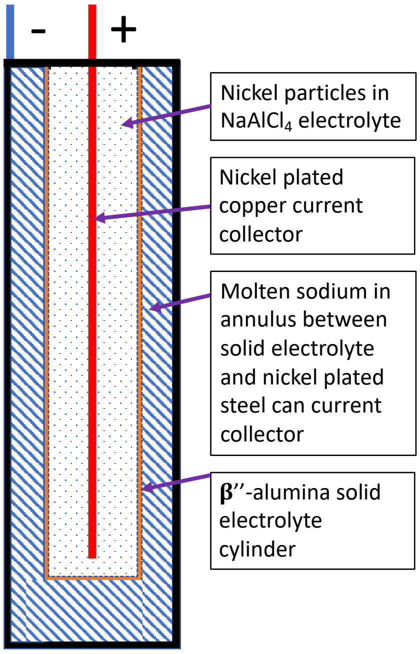

Figure 2. Cell configuration of the ZEBRA battery. Dustmann (2004).

$NiCl_2 + 2Na = Ni + 2NaCl$ …..1

A sodium aluminium chloride secondary electrolyte is added to the positive electrode to enhance ionic conduction to the nickel particles. It also introduces the remarkable feature that in the case of breakage of the solid electrolyte of a cell in a series stack, that cell would be shorted by the aluminium formed when the sodium metal contacts the electrolyte as shown in Equation 2. The battery would still function albeit at a slightly diminished potential considering typical battery potentials of >250 V.

$Na + NaAlCl_4 = Al + 4NaCl$ …..2

The main drawback of this technology is the minimum and optimal functioning temperatures of, respectively, ~270 and 300°C. Continuous operation with overnight charging and daytime discharging fits in well with the need to keep the battery hot. Numerous challenges were resolved and production techniques developed, such that a major production facility for the battery was established in Switzerland in 2004 with an initial capacity of 2000 batteries per year (Dustmann, 2004).

The ZEBRA-battery has attractive features such as a 100% coulombic efficiency, energy efficiency ~90% and long life (>3000 cycles) but a relatively low specific power of ~ 170 W/kg. Sudworth (2001) reported trials with ZEBRA-batteries in land and marine mobility applications and for backup power in telecommunications. It is presently still commercially available and being evaluated (Veneri *et al.*, 2017; Shamim *et al.*, 2021) but less attractive, due to its high temperature operational requirement, relatively low power and energy densities, and relatively high cost as the advantages of scale were never achieved.

All vanadium flow battery

Redox flow batteries (RFB) store and release energy available in facile redox couples of dissolved species in electrolytes stored in external reservoirs. Energy is cycled by circulation of the electrolyte through the electrochemical cell as required to support the electrochemical reactions as schematically shown in Figure 3. This arrangement allows for the independent scaling of the energy present in the volume of the stored electrolytes and the power defined by the area of the electrodes and the overpotential windows available for charging and discharging at high coulombic efficiencies. Many redox couples have been investigated for use in RFBs but only a few such as the iron-chromium, zinc-chlorine, zincbromine, all-vanadium and bromine-polysulfide have been developed up to commercialisation (Leun *et al.*, 2012).

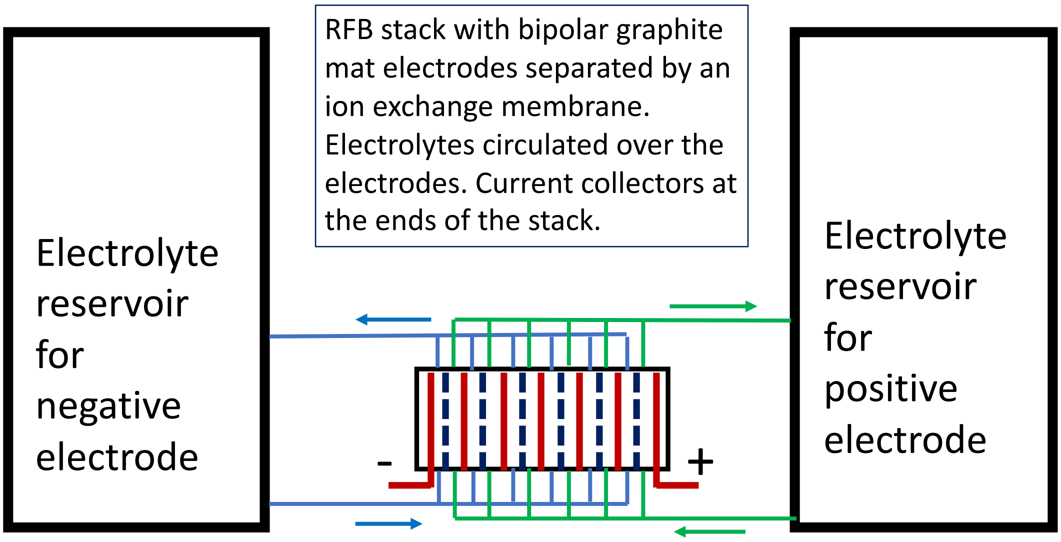

Figure 3. System configuration of the all vanadium flow battery.

The all-vanadium system is of importance to South Africa considering our very significant vanadium ore reserves and processing capabilities. The suitability of an aqueous vanadium sulfate electrolyte for such a system may be established using the Pourbaix diagram, and taking into consideration that only dissolved species should be involved in half cell reactions; with potentials aligned with the stability region of water. Inspection of the diagram for the V-H_2O system shown as Figure 4 indicates that this may be achieved at high acid concentrations with the cell reaction shown as Equation 3.

$VO_2^+ + V^{2+} = VO^{2+} + V^{3+}$…..3

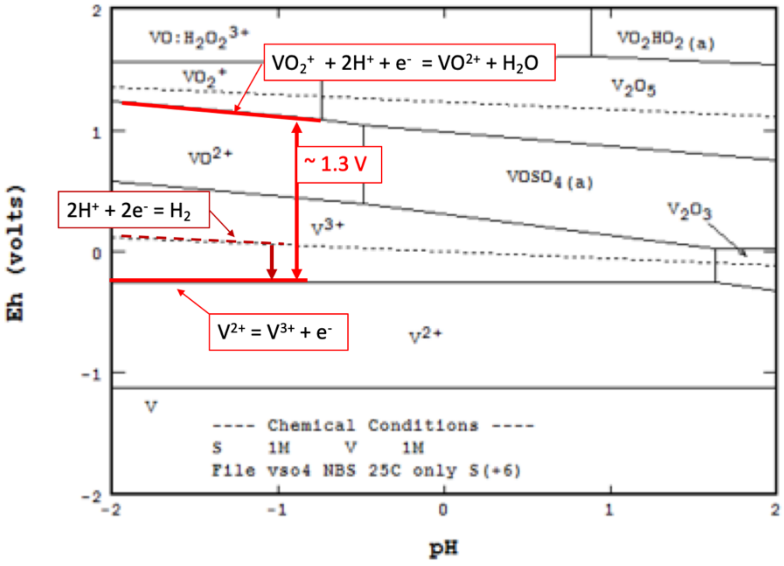

Figure 4. Pourbaix diagram for vanadium in aqueous sulfate at 25°C constructed using the NBS database considering only sulfate. Suitable conditions and characteristics for the all vanadium flow cell are indicated.

The half cell reactions indicated on the diagram involve only single electron transfers and are thus likely to be kinetically attractive, but the cell potential is a rather modest ~1.3 V. The operating potential window of the cell is near that of water but the coulombic efficiency of the cell might be reduced if the thermodynamically favoured reduction of hydrogen ions to hydrogen gas occurs at a significant rate, as indicated. The need to separate the anolyte and catholyte in the electrochemical cell by means of a relatively sophisticated ion selective membrane able to handle the highly acidic and oxidising electrolyte adds significant complexity and cost to the RFB. The same carbon based electrode material, such as graphite based felt and current collectors, is often suitable for both redox couples and may then be used as bipolar electrodes arranged in a simple series stack with electrolyte feeds to the individual half cells but with current offtakes only at the ends of the stack. The expected long life of a vanadium redox flow battery (VRFB) and the direct recyclability of most of the components and electrolyte makes the VRFB attractive from an environmental point of view, especially if used for applications with high energy to power requirements (Weber *et al.,* 2018).

An energy efficiency of 83% is quoted for an all-vanadium RFB operating at 300 A.m^{-2} at 35°C (Leung *et al.*, 2012) but this should be compared to the similar figure determined for the positive electrode alone (Flox *et al.*, 2015) indicating that a roundtrip energy efficiency of ~ 75% would be more realistic (Kear *et al.*, 2012). The energy density achievable with the all-vanadium RFB is rather low at 25 Wh.kg^{-1} compared to the 280 Wh.kg^{-1} of the NMC622 lithium ion battery (Leung *et al.*, 2012; Volkswagen, 2018) due inter alia to the ~ 2M solubility limit of the vanadium species in the sulfate electrolytes (Skyllas-Kazakos *et al.,* 2016), single electron half cell reactions, and pumping requirements. The VRFB would thus be most suitable for daily cycling in high energy to power ratio applications. The prospects for the wider application of VRFB would be favoured by reducing the cost of the electrolyte and membranes, and by improving the roundtrip energy efficiency.

Lithium ion batteries

Lithium is an attractive element to utilise for achieving high power and energy densities in batteries, due to its low density, small ionic size and high reactivity. The successful use of lithium, however, require a non-aqueous electrolyte with high ionic conductivity and lithium ion transport rate, and a stability window to allow a large operating potential window and cell potential generated by a matching positive electrode. Typical mobile applications further require rechargeability at high energy efficiencies over many cycles, high volumetric and mass energy densities available at high potentials, charge retention, a low price and good recyclability. Reversible metal plating and dissolution while maintaining a flat surface is a major issue to resolve and has to date not been achieved on a commercial scale (Liu *et al.,* 2019). The development of lithium ion insertion half cells such as the graphite-based negative and transition metal oxide-based positive electrodes avoid this problem but significantly reduce the power and energy densities achievable.

The performance of the present generation LIB is truly remarkable with energy densities of up to ~300 Wh.kg^{-1}, energy efficiencies of ~90%, minimal self-discharge and extended cyclic lives ranging from ~500 to ~5000 cycles depending on the type of LIB. Potentially lucrative innovations to further improve the fast charging capabilities, safety, power and energy densities, or alternative chemistries are actively pursued by many researchers (Liu *et al.,* 2019; Ma *et al*., 2021). An interesting innovation that received significant backing is the use of a ceramic solid state electrolyte separator that allows for the plating of lithium metal and thus fast charging and delivery by preventing lithium metal dendrite penetration to the positive electrode (Quantum Scape, 2022).

LIB is presently the system of choice for mobile energy storage and has benefitted significantly from the large scale adoption of the technology that allowed for more efficient mega-manufacturing facilities to further drive down costs. It is expected to be the short and medium dominant technology and will challenge the position of other technologies in niche applications as LIBs cascade down from more demanding mobile applications rather than being recycled.

Supercapacitors

Conventional capacitors are used for the fast storage and release of energy over many cycles but has found limited application in electrical energy storage as such, due to their limited storage capacity of less than 1 Wh.kg^{-1}. Supercapacitors have significantly higher capacities of ~ 10 Wh.kg^{-1} achieved by augmenting the charge storage in double layers with so called pseudocapacitance involving surface and near-surface reversible faradaic reactions (Fleischmann *et al.,* 2020). Hydrated ruthenium oxides in acid electrolytes exhibit a high degree of pseudocapacitance, probably due to fast hydronium transfer along hydrated grain boundaries with charge flow due to partial reduction of ruthenium and supported by the electron conductivity of the ruthenium oxide. Manganese dioxide similarly exhibits relatively high pseudocapcitance in neutral electrolytes but with the capacitance limited by poor electron conductivity (Vangari *et al*., 2013; Fleischmann *et al*., 2020). Strong growth in the development of supercapacitors is predicted especially considering hybrid devices combining the high power storage and delivery of supercapacitors with the lower but still relatively high capabilities of near surface intercalation batteries. These devices could buffer the power surges delivered by regenerative braking as already used on electric trains (Sahin *et al*., 2022). As with other energy storage devices, the wider application of the technology hinges on cost with many alternative materials and production methods being investigated.

Prospects for Southern Africa

South Africa has a relatively small but innovative research community that contributed significantly to the early development of the high temperature ZEBRA battery. The present challenge is to make meaningful contributions in terms of materials for LIB, which is predicted to create significant demand for high purity lithium, cobalt, nickel and manganese (WEF, 2019). Strong growth is also predicted for supercapacitors with commensurate growth in materials with near surface faradaic exchange capabilities such as ruthenium oxide and other transition metal-based materials. An obvious strategy would be to leverage the existing expertise in extractive metallurgy to develop processes and support to enable competitive production of relatively pure products based on the large resource base of cobalt, nickel, manganese and PGMs in Southern Africa. The potential for further processing into high value active materials could be enhanced and supported by research of layered materials suitable for near-surface and bulk intercalation reactions, and the more efficient use of PGM in supercapacitor materials to enable the use of high value PGM in more cost sensitive applications. South Africa has facilities for the manufacturing and recycling of LAB but not for LIB. The case for a manufacturing facility for LIB cells is not obvious, considering the large scale required for a viable facility and the relatively small local market. The production of LIB battery packs to support solar and wind generation is alreadydone, and could be developed to also include automotive applications (TIPS, 2021).

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