# Availability of Suitable Raw Materials Determining the Prospect for Energy Storage Systems Based on Redox Flow Batteries

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Successful large-scale deployment and manufacturing of newly designed products depends on the availability of raw materials and therefore even fundamental research on electrochemical energy sources cannot ignore the need to secure enough construction and active mass materials. Increasing use of renewable energy sources (for example, wind and solar) require some means of energy storage to balance fundamentally periodic or irregular energy supply. This storage can be electrochemical. One of the most interesting types of electrochemical cells suitable for energy storage are the so-called redox flow batteries (RFB) that store energy in reservoirs. Unlike in conventional cells and batteries, where the amount of stored energy directly depends on the size or volume of the battery electrodes, in the flow cells the advantage is that their energy capacity can be adjusted by refilling the connected containers. The paper describes the basic principles, design and types of flow systems, as well as interesting modern developmental trends related, among other things, to the availability, supplies, mining and market prices of raw materials used in these storage devices. The present concept of RFB is based on utilisation of various oxidation forms of vanadium. However, since the world supplies of vanadium are limited and unsuitable to meet the whole theoretical demand for energy storage, other concepts, based on more common metals (zinc, lead) or organic redox systems, are being discussed.

Key words: global ore resources, redox reactions, energy storage, flow cells, RFB, accumulators, raw material market

#### Introduction

Unlike the fundamental limits of electrochemical power sources, which are based on thermodynamic data and are well understood, prediction of the viability of mass production of a battery with particular chemistry requires sufficient supplies of chemical and raw materials that may not be known with high certainty. While data on available minerals exist, they have a large uncertainty error bar, and the availability is also driven by demands. If the demand for a particular material increase, the willingness to pay a premium for extraction may bring to market resources previously thought non-viable (Fletcher, 2011; Takaya et al., 2018). For example, lithium metal availability and its perceived shortage or abundance have been a study of a number comparisons, for example, (Gruber et al., 2011) and current news economy considerations (Patterson and Gold, 2018). In a rare case, as happened with mercury (Vanýsek, 2015), the demand may also decrease. Here we will look at a type of a battery that relies on utilising reduction and oxidation of metal salts, for example, vanadium. Hence, its commercial success depends on the ability to produce enough vanadium salts, presumably by tapping the materials available in the Earth crust.

The energy of chemical bonds is a very advantageous way of storing energy. Combustion is historically (and even prehistorically) the most significant way of releasing energy in the form of heat. However, thermal energy is less advantageous for energy supply than electrical energy. For this reason, it would be better to convert the chemical energy of bonds directly into electrical energy. This is possible in electrochemical sources, both in the primary cells, that are discarded after use, and secondary ones, which can be recharged after use, and in particular in fuel cells, which are electrochemical sources whose own active substance is not the part of the conversion cell, but is stored in external containers. The active substances and their choice in the flow cells are significantly and actively influenced by the raw materials used as the basis of the redox pairs.

With increasing efforts to use renewable sources as a source of energy, there is a new practical complication, especially for solar cells and wind generators, namely that these energy sources are working intermittently and to some extent unpredictably (Tauš et al., 2015). It is therefore preferable, on a global scale, that electricity should be stored at times when it is overproduced and then made available at times when the demands for energy is higher than the supply from these sources. So far the most efficient storage systems are mechanical, of which the most advantageous are both pumping hydroelectric power plants and compressed air storage (Vanýsek et al., 2015). However, these systems are only effective if they are designed for high performance, requiring substantial initial investment, and physically cannot be placed everywhere. On the other hand, retention of energy in electrochemical cells of the second type (rechargeable batteries) is an obvious choice, and from the point of view of known technologies, it is quite possibly even the most practical method. The task of science and research is to find batteries that will be reliable and generally financially and practically

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available with good technical parameters. This article discusses one type of an electric accumulator, the so-called redox flow battery.

#### The principle of the redox flow battery

The expression "redox" is derived from joining two words, reduction and oxidation, implying the simultaneous occurrence of both of these processes, oxidation, loss of electrons and reduction, the gain of electrons. From the general electrochemical point of view, where the overall charge balance is thermodynamically required, any electrochemical system will be a "redox" system. However, in the vernacular of electrochemical power sources, the redox flow battery was adopted for a particular concept of electrochemical energy storage.

A redox flow battery (often abbreviated RFB) describes a power source that uses for energy generation two solutions, one in an oxidised form, the other in a reduced form. During the release of energy the solutions react on electrodes, the first is reduced, and the other is oxidised and on the outside connected the circuit between the two electrodes flows electric current. During the process of charging the function of oxidation and reduction is reversed and the system is charged from an external energy source.

The principle of the flow redox cells is the same as the principle of any galvanic cell. Oxidation and reduction, occurring simultaneously, but in separate half-cells, cause the flow of an electric current, carried by ion flow in the electrolyte of the electrochemical cell and by electrons in the external electric circuit. This electric current is then the source of energy where it is needed. Compounds that undergo oxidation or reduction are sources of chemical energy. When these substances are reacted, the electrochemical cell is discharged. For rechargeable (secondary) cells, the discharge process can be reversed, and the cell again recharged via an external power source. Reactive substances pass into their original form during charging. However, the redox flow cells differ from the conventional electrochemical cells by the fact that the reacting material is not part of the construction of the cell, but it is supplied from external storage tanks in the form of electrolytes which, during cycling, pass from the charged to the discharged state. The total energy capacity of the system is proportional to the amount of electrolytes in the external reservoirs, while the output power is dependent on the electrode arrangement (the surface of the electrode system). In a sense, the behaviour of the flow cell, when delivering energy, is identical to the fuel cell operating principle. However, the fuel cell is not expected or designed to reverse the current flow and recharge the system again. The diagram of the redox flow cell showing its principle is given in Fig. 1 and a real commercial cell is depicted in Fig. 2.



Fig. 1. A diagram of a redox flow battery.



Fig. 2. An actual commercial vanadium flow cell. The left and right upper containers in the transport cages hold the respective vanadium solutions. The middle is the armature of the electrochemical cell. The containers and the cell are placed over the blue reservoirs intended to capture any spill in case of an accident. For sizing an Estwing 22, a 13" geological hammer, is leaning against the middle retention reservoir.

#### Advantages and disadvantages of the redox flow batteries

The greatest advantage of redox flow cells is that the parts defining the power and energy parameters are physically separated from one another. Their design can then be very variable depending on the needs and applications. A need to increase the cell capacity can be solved by increasing the volume of electrolyte storage tanks. Alternatively, by supplying a new electrolyte, the cell can be quickly "charged." If less power is sufficient, smaller cell size can be constructed. Then, for greater performance, it is possible to design larger cells or use several smaller modules. Since the cell electrodes do not change chemically during charging and discharging (at least in theory), the number of possible operating cycles is theoretically endless. Other benefits include the ability to respond quickly to network requirements, minimal maintenance, or zero emissions. These cells are also characterised by short-term overloading tolerance or the possibility of replenishment of energy by exchanging the storage containers.

Compared with other common types of batteries (for example, Li-ion), the RFB power and energy density are very low. This makes the cells unsuitable for mobile and traction applications. Accordingly, for larger nominal currents, the active surface of the electrodes must increase. This results in a high concentration gradient of electrolyte flowing through the cell, resulting in the reduction of an average current density. Compared with conventional batteries, flow cells are more complicated and require additional support devices such as mechanical pumps, sensors, control units, additional tanks, and the like.

**Early beginning.** The idea of a flow-cell battery was first mentioned in 1933 in P. A. Pissoort's patent, which also described the use of a vanadium redox pair (Pissoort, 1933). On the basis of US patent (Thaller, 1976) research was carried out in the 1970s by NASA regarding such cells. At first, the systems of redox pairs of Fe-Cr (Ponce de León et al., 2006) and Fe-Ti (Savinell et al., 1979) (soluble salts of Fe, Cr, and Ti in aqueous HCl) were studied. The reactions for the first system can be described as follows:

$$Fe^{2+} \xrightarrow[\text{Discharging}]{Charging}} Fe^{3+} + e^{-}$$
(1)

Negative electrode 
$$Cr^{3+} + e^{-} \xrightarrow{Charging}{Discharging} Cr^{2+}$$
 (2)

Positive electrode

The open circuit potential of this cell (OCV) was about 1.18 V.

The reactions of the second mentioned couple were:

$$Fe^{2+} \xrightarrow[Discharging]{Charging}} Fe^{3+} + e^{-}$$
(3)

Negative electrode

$$Ti^{4+} + e^{-} \underbrace{\underset{\text{Discharging}}{\overset{\text{Charging}}{\longrightarrow}}} Ti^{3+}$$
(4)

This system exhibited somewhat higher open circuit potential (1.19 V) than the Fe-Cr scheme. However, the current density was low, only about 14 mA·cm<sup>-2</sup>, compared to 20 mA·cm<sup>-2</sup> of the first system. This type of a cell was using the solution of 1.0 mol·dm<sup>-3</sup> TiCl<sub>3</sub> in 3.5 mol·dm<sup>-3</sup> HCl on the negative side and 1.0 mol·dm<sup>-3</sup> FeCl<sub>3</sub> in 3.0 mol·dm<sup>-3</sup> HCl on the positive side.

**Practical system - a system with vanadium salts.** In 1978, A. Pellegri and P. M. Spaziante filed a patent application in which they introduced the idea of using vanadium (Pellegri and Spaziante, 1983). However, they did not become involved in another major development. The first known and commercially successful demonstration of the vanadium cell was presented in 1986 by a group of Australian scientists led by M. Skyllas-Kazacos of the University of New South Wales (Skyllas-Kazacos et al., 1986). This success awakened a Japanese interest in flow systems. In 1989, the development of vanadium redox batteries intensified, utilising the experience gained in developing Fe-Cr systems. In 1996-2000, testing systems emerged, and the first commercial installation was launched in 2001.

The vanadium redox batteries (VRB) concept is particularly interesting because it is based on the use of two different salts of vanadium dissolved in an acidic environment. Vanadium exists in several valences, and the two electrochemical half-cells forming the resulting cell are based on the use of different valence state compounds of the same element. The added advantage of this concept is that in the event of accidental mixing of both solutions no irreversible depreciation of the stock solutions will happen. The negative side is using the redox reaction of vanadium  $V^{2+}/V^{3+}$ , and the positive side is the reaction  $V^{5+}/V^{4+}$ . The typical solutions of vanadium salts are 1.6 - 2.0 mol·dm<sup>-3</sup> in 2.0 mol·dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. The reactions during charging and discharging on the two electrodes follow the scheme:

Positive electrode 
$$VO^{2+} + H_2O \xrightarrow[bischarging]{Charging} VO_2^+ + 2H^+ + e^-$$
 (5)

Negative electrode

$$V^{3+} + e^{-} \underbrace{\underset{Discharging}{\overset{Charging}{\longleftarrow}}}_{V^{2+}} V^{2+}$$
(6)

If the two electrolytes were mixed together, they would react, releasing energy, but in the form of heat. Therefore, to obtain electrical energy instead of heat, the two electrode chambers are separated by a membrane, which allows passage of only one kind of ions. In the case of VRB, it allows transport of hydronium ions  $H^+(or,$ more correctly  $H_3O^+$ ), which travel between the chambers of the positive and the negative electrode. The presently used membrane is NAFION manufactured by DuPont. Considering the cost of the fluorosulfonate polymer NAFION, a VRB large-scale deployment is debatable. Therefore, one of the aims of the battery research is finding more economical membrane separators. The potential of a fully charged cell without load (OCV - Open Circuit Potential or Voltage) is about 1.6 V for the system of half-cells based on vanadium (II) and (V), each with vanadium concentration of 2.0 mol·dm<sup>-3</sup> in 2.0 mol·dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> (Skyllas-Kazacos et al., 1986). The energy density of the 2.0 mol dm<sup>-3</sup> vanadium electrolytes is around 25 Wh kg<sup>-1</sup> (Skyllas-Kazacos et al., 2011), the current density can reach 10 to 130 mA cm<sup>-2</sup> depending on the system configuration, which can operate in the temperature range 10-40 °C (Skyllas-Kazacos et al., 1999). Any of these parameters should be regarded as approximate. The so-called standard potential available form tables is an equilibrium value at standard conditions, which are a defined temperature and pressure, but most importantly, also unit activities of all the participating reactants, which are not just the redox pairs, but in the case when protons enter the reaction, even the activity of the acid enters into the play. For example, Alotto (Alotto et al., 2014) gives as the standard VRB potential  $E^{\circ} = 1.26$  V at 25 °C, but the practical equilibrium (pseudo) standard potential is  $E^{\circ} = 1.4$  V, which confirms, for example, Buckley (Buckley, 2016). The concentrations in practical cells must be as high as possible (higher energy density). For the thermodynamic calculation, the activities would have to be unity and the same for the cathodic and anodic half-cell, which is the situation for a half-charged cell. Therefore, the charged cells will have higher potentials than the standard values; the discharged cells will have, of course, lower potentials.

One advantage of the vanadium cell is also the fact that the colours of the various oxidation states in a sulfuric acid solution of vanadium are very distinct, yellow for  $VO_2^+$ , pale blue for  $VO^{2+}$ , green for  $V^{3+}$  and purple for  $V^{2+}$ . This can be used for example in assessing spectrometrically the state of charge of the VRB (Buckley et al., 2014).

The energy density of the system with vanadium salts on both sides of the electrochemical cell is relatively low. Therefore, research has focused on modifying these systems to increase the density and, above all, to find an alternative to poorly available vanadium. Therefore, systems are developed where the vanadium salt is replaced by another variant of the positive half-cell chemistry. These are, for example, V-Br, V-Mn, V-Ce systems, V-glyoxal (O<sub>2</sub>), V-polyhalide and others. At present, the best parameters are still available with vanadium salts on both sides, followed by the vanadium-bromine system. However, it is assumed that further development of suitable electrodes, membranes and electrolytes will improve the parameters of alternative vanadium-based systems. In the event of higher energy efficiency, higher energy density, lower prices, or a larger range of working temperatures, future deployment of these systems as energy storage could be considered.

An interesting variant of a vanadium flow cell is the so-called vanadium-oxygen redox fuel cell (VOFC) (Menictas and Skyllas-Kazacos, 2011). Here is even the description "fuel cell" in the name. In this system, the positive half-cell consists of a gas diffusion electrode using oxygen from the air. This saves weight and volume of the system, one electrolyte tank and half of the support technologies. On the other hand, a relatively large amount of platinum-based catalysts is required for the construction of the gas diffusion electrode. The chemical reactions are as follows:

Positive electrode 
$$2H_2 O \xrightarrow[Discharge]{Charging}{Discharge} 4H^+ + O_2 + 4e^-$$
 (7)

Negative electrode

$$4V^{3+} + 4e^{-} \underbrace{\xrightarrow{Charging}}_{Discharge} 4V^{2+}$$
(8)

and the OCV of the cell is  $E_o = 1.0$  V. Due to the absence of the entire single electrolyte subsystem, the energy density of this solution is substantially increased. It is to be noted, however, that in the systems using oxygen (air) it is tacitly assumed an unlimited source of air is available, which in some cases (for example on submarines) may not be true.

Practical applications of the vanadium systems exist, and the total installed capacity of the VRB in the world is 18 MW in 24 different locations. The largest storage site is currently located in Japan in Osaka, which has 3 MW output power at 16 minutes of discharge.

### Modern systems and future development

Vanadium salts are relatively expensive, not available on a large-scale, and relatively rare, considering that the primary use is of vanadium metal (92 % of total production) in steel manufacturing (Kudelas et al., 2014). The mining is heavily centred on the Asian countries, as shown in Fig. 3.



Fig. 3. Production of vanadium (USGS, 2017).

Given this, the current development is focused on the search for other attractive redox cell systems utilising more readily available raw materials with lower cost and high solubility in aqueous solutions. A detailed overview of modern trends is, for example, presented by Skyllas-Kazacos and her colleagues (Skyllas-Kazacos et al., 2011) in a review from 2011 and the newest results are summarised in a review from 2016 (Ulaganathan et al., 2016). Another fundamental shortcoming of the vanadium cells lies in the corrosive nature of the necessary sulfuric acid electrolyte. While the vanadium cells were those first studied and put into operation, there are other promising chemical principles that represent the most modern approaches, possibly with a high risk of failure but also with a high potential reward.

System Zn-Br. One such modern cell uses zinc and bromine chemistry, which gives the cells higher energy density (mainly due to a solid zinc phase) than the vanadium-based system has. It is a so-called hybrid system that differs from conventional flow batteries in that at least one of the redox pairs is not fully soluble. The electrolyte on the anode side is aqueous, and the electrolyte on the cathode side also contains an organic amine, which contributes to greater solubility of bromine. During charging, solid metal zinc is deposited on the anode, while the bromide ions are oxidised to *liquid* bromine, which forms on the opposite electrode. The concept of such a battery was described more than a hundred years ago (Bradley, 1885), nevertheless not until 1970-1980 Exxon a Gould suggested a practical use (Butler et al., 2000; Putt and Attia, 1982). Demonstration hybrid systems exist in the size of 50 to 400 kWh, which can supply energy for 2-10 hours with the efficiency of 70 % and more (Linden, 1995; Butler et al., 2000). The energy density is about 65–75 Wh kg<sup>-1</sup> (Linden, 1995). An even more recent concept was designed in the Pacific Northwest National Laboratory (PNNL) by a team led by Wei Wang (Li et al., 2015; Wei et al., 2015). This concept is based on zinc and polyiodide. Some of the problems of the bromine-zinc battery are the cost of electrodes, material corrosion, the formation of metal dendrites during the deposition of zinc during charging, which may lead to a cell short-circuit, significant selfdischarge, unsatisfactory energy efficiency, relatively short service life (Ponce de León et al., 2006) and not the least that bromine, if released into environment, can be hazardous. The cells with metal deposition also have in general lower number of useful cycles.

The undeniable advantage of zinc over vanadium is, however, its price, which is steadily on the average only 10 % of the price of vanadium (Fig. 4) (USGS, 2017).



Fig. 4. Comparison of prices of zinc and vanadium (Infomine, 2017).

An obstacle to overcome is that in zinc cells, the amount of zinc deposited on the surface of the negative electrode grows over time through the diaphragm or membrane separator, thereby reducing the efficiency of the battery.

**Flow-through cells with organic electrolytes**. In the paper (Janoschka et al., 2015) is described a redox flow-through cell which is based on such materials as the ion-radical TEMPO (2,2,6,6-tetramethyl-piperidin-lyl)oxyl or viologen. The advantage of such an arrangement is that no corrosive solvents are used, and therefore cheaper membranes can be used in the construction of the cells. The proposed organic materials are synthetic and, in principle, should the proper technology be developed, they could be produced in considerable quantities. Due to the novelty of this cell, its shortcomings or possible problems are still unknown. Generally, the biggest problem with non-aqueous redox cells will be the availability of the solvents that promote high stability of the active material. The capacity of the cell is directly proportional to the solubility of the active material. Aziz and co-workers (Huskinson et al., 2014) described a new concept of the flow cell based on organic molecules quinones. Abruña et al. (Potash et al., 2016) came with an idea how to use in a flow cell a single kind of organic

molecule, but one that exists in both the oxidised and reduced form. An example can be diaminoanthraquinone. An advantage of such an arrangement is that it is possible to design a membrane-free system relying only on laminar flow which does not allow spontaneous mixing of the two electrolytes in contact.

**Flow-through lead battery.** Another interesting concept of the flow-cell battery is the so-called lead-acid battery (Nandanwar and Kumar, 2014; Hazza et al., 2004; Pletcher and Wills, 2004). The schematic representation is shown in Figure 5. Unlike the conventional lead-acid battery (lead and sulfuric acid solution), it uses the highly soluble form of divalent lead Pb(II), which is supplied in the form of an electrolyte for both half-cells, for example as lead methanesulfonate in concentration up to 2.5 mol·dm<sup>-3</sup>. During charging, lead is deposited from this electrolyte on the negative electrode and lead oxide on the positive electrode. Electrode reactions occur according to the scheme:

Positive electrode: 
$$Pb^{2+} + 2H_2O \underset{Discharging}{\xleftarrow{} Charging} PbO_2 + 4H^+ + 2e^-$$
 (9)

Negative electrode  $Pb^{2+} + 2e^{-} \xrightarrow[bicharging]{Charging} Pb$  (10) The OCV cell is approximately 1.62 V. Several systems, such as perchloric acid, hydrochloric acid,

The OCV cell is approximately 1.62 V. Several systems, such as perchloric acid, hydrochloric acid, hexafluorosilicic acid or tetrafluoroboric acid, have been studied as a suitable electrolyte that dissolves the lead salts. At present, a methanesulfonic acid is used, which ensures good solubility of divalent lead and sufficient stability of the deposited solid lead and lead oxide.



Fig. 5. Schematic depiction of the lead flow battery.

Because the electrolyte solution is the same for both half-cells, it is not necessary to use an ion exchange membrane and, at the same time, the concept requires only a single electrolyte reservoir. This greatly reduces the cost and structural complexity of the cell. Problems encountered in this type of a cell are closely related to phase changes on the electrodes during cycling and are typical of systems where metal deposition occurs. While the anodic deposition of PbO<sub>2</sub> layers takes place relatively simply, the lead deposition to form a compact layer leads to a formation of dendrites around the edges of the negative electrode, which can cause the cell to short. Problems are also related to poor adhesion of the PbO<sub>2</sub> layer to the support collector. These problems could be addressed by the addition of suitable additives, which is the subject of current research in this field (Collins et al., 2010; Chen and Chang, 2015).

**Chemically regenerated redox fuel cells.** A chemically regenerated redox fuel cell is a type of fuel cell that uses a redox pair solution as an electron mediator for fuel and oxidant reaction. Thus, the chemically regenerated redox fuel cell is also a kind of flow electrochemical cell because it has two redox pair solutions flowing along the electrodes. Following a subsequent electrochemical reaction on the electrodes, these solutions are taken to regeneration reactors where they are re-reduced or oxidised by a reducing or oxidising agent. After

regeneration, the solutions circulate again along the electrodes, and the cycle continues. Compared to the flow cells described here in the previous chapters, however, charging or regeneration takes place outside of its own central electrochemical cell. The first results on redox fuel cells were written by Kummer and Oei (Kummer and Oei, 1982; Oei, 1982; Kummer and Oei, 1985), whose work has shown both advantages and limitations of the redox fuel cell. The main attraction of this concept is to avoid catalysts on the surface of electrodes and the use of simple (cheap) electrode materials. Hydrogen gas can be used to reduce the need for regeneration (charge). However, the main disadvantage of using hydrogen to regenerate the negative half-cell is a relatively high potential for the reversible redox pair of hydrogen, which limits the choice of redox pairs that would be suitable for the negative half-cell. Oxidation regeneration should be possible with air oxygen. Unfortunately, even here in further studies, it was shown that the oxidative regeneration of the positive half-cell is kinetically slow and requires relatively expensive catalysts, which negates the main purpose of this approach. Kummer and Oei were looking for a suitable approach for electric cars (Kummer and Oei, 1982; Kummer and Oei, 1985). Other researchers (Ferrigno et al., 2002) evaluated various alternative membranes for these cells. Recent work has been devoted to research into a cell in which methanol is used as fuel (Ilicic et al., 2010; Moraw et al., 2007).

The aspect of global resources is constructing redox flow cells. The path from laboratory design to a useful mature product is described by the technology readiness level (TRL), from Level 1 (Basic Principles observed and reported) to Level 9 (Actual application in its final form). While many of the battery technologies are or will be proven through successful operations, it does not mean the batteries would be suitable for truly large-scale production relevant for energy production and storage.

The primary power demand on Earth has been in 2015 18 TW (BP, 2016), with 78 % produced from the fossil fuels. As the focus on renewables grows, so does demand on new technology, but power generation (e.g., wind, solar) and energy storage. Deployment of these new technologies will require a shift towards new materials and unprecedented demand for mineral resources.

While the elemental abundance of elements in Earth crust may provide some guidance to mineral availability, it is rather skewed guidance. From the planning point of view, the elements that tend to concentrate into ores with sufficiently high concentration to allow mining are those that will be promising for large-scale technology.

Due to fluctuations of power supplied by solar and wind energy, some of it needs to be stored. If we assume that today's energy production is 10 % derived from wind and solar and it would be desirable to store 20 % of that, it would represent 0.36 TW of power, and assuming a 24-hour cycle; it would correspond to storage of  $3x10^{16}$  J of energy. Since a lead–acid battery has energy density about 140 kJ·kg<sup>-1</sup>, if the above storage were solely depended on lead, then the amount of lead required would be about  $2.1x10^{11}$  kg. Considering that present yearly production of lead is about  $4x10^9$  kg, the needed amount of lead corresponds to about 50 years of production. For a vanadium redox flow, with the density about 54 kJ·kg<sup>-1</sup>, about 5.6x10<sup>11</sup> kg of vanadium would be needed. This brings up to the forefront the issue of a mass-specific problem. In this scenario, the amount of vanadium corresponds to about 8800 years of present yearly production (Vesborg and Jaramillo, 2012).

## Conclusion

Considering that many commercial vanadium and other redox cells already exist and there is no doubt that there is a need to store excess electricity and that there is a lack of suitable energy storage alternatives (pumping hydroelectric power plants and compressed air storage), the development of VRB is timely. Future electrochemical storage of energy has already almost achieved success as commercial systems are available for purchase. Ultimate success will depend on which technology or concept will be chosen as the most advantageous, and this choice may not even be the same in all geographic and economic areas. Since the first models of industrial flow cells are already installed, there is no doubt that there will be future demand for such systems. Current cells based on vanadium cannot singularly meet this demand, as the fundamental redox material is not sufficiently common and would not be affordable even on a large-scale. This will require shifting to other materials. If such cells are developed, it is almost guaranteed that they will be profitable and economically successful.

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#### References

- Alotto, P., Guarnieri, M., Moro, F. (2014) Redox flow batteries for the storage of renewable energy: A review. *Renewable and Sustainable Energy Reviews*, 29, 325-335.
- BP (2016) BP Statistical Review of World Energy June 2016.
- Bradley, C.S. (1885) Secondary Battery. US312802 A patent application.
- Buckley, D.N. (2016) 7 March 2016. RE: Personal Communication.
- Buckley, D.N., Gao, X., Lynch, R.P., Quill, N., Leahy, M.J. (2014) Towards Optical Monitoring of Vanadium Redox Flow Batteries (VRFBs): An Investigation of the Underlying Spectroscopy. *Journal of The Electrochemical Society*, 161, A524-A534.
- Butler, P.C., Eidler, P.A., Grimes, P.G., Klassen, S.E., Miles, R.C. (2000) Zinc/Bromine Batteries. Sandia National Laboratories.
- Chen, H.Y., Chang, C.W. (2015) Towards Long Cycle Life of Soluble Lead-Acid Redox Flow Batteries, Meeting Abstracts. *The 227th Meeting of the Electrochemical Society*. Chicago: The Electrochemical Society.
- Collins, J., Kear, G., Li, X., Low, C.T.J., Pletcher, D., Tangirala, R., Stratton-Campbell, D., Walsh, F.C., Zhang, C. (2010) A novel flow battery: A lead acid battery based on an electrolyte with soluble lead(II) Part VIII. The cycling of a 10 cm × 10 cm flow cell. *Journal of Power Sources*, 195, 1731-1738.
- Ferrigno, R., Stroock, A.D., Clark, T.D., Mayer, M., Whitesides, G.M. (2002) Membraneless Vanadium Redox Fuel Cell Using Laminar Flow. *Journal of the American Chemical Society*, 124, 12930-12931.
- Fletcher, S. (2011) Critical Matter. Popular Science, 2011 June, 76-110.
- Gruber, P.W., Medina, P.A., Keoleian, G.A., Kesler, S.E., Everson, M.P., Wallington, T.J. (2011) Global Lithium Availability. *Journal of Industrial Ecology*, 15, 760-775.
- Hazza, A., Pletcher, D., Wills, R. (2004) A novel flow battery: A lead acid battery based on an electrolyte with soluble lead(ii) Part I. Preliminary studies. *Physical Chemistry Chemical Physics*, 6, 1773-1778.
- Huskinson, B., Marshak, M.P., Suh, C., Er, S., Gerhardt, M.R., Galvin, C.J., Chen, X., Aspuru-Guzik, A., Gordon, R.G., Aziz, M.J. (2014) A metal-free organic-inorganic aqueous flow battery. *Nature*, 505, 195-198.
- Ilicic, A.B., Wilkinson, D.P., Fatih, K. (2010) Advancing Direct Liquid Redox Fuel Cells: Mixed-Reactant and In Situ Regeneration Opportunities. *Journal of The Electrochemical Society*, 157, B529-B535.
- INFOMINE. (2017) Commodity Charts [Online]. Available: http://www.infomine.com/ChartsAndData/.
- Janoschka, T., Martin, N., Martin, U., Friebe, C., Morgenstern, S., Hiller, H., Hager, M.D., Schubert, U.S. (2015) An aqueous, polymer-based redox-flow battery using non-corrosive, safe, and low-cost materials. *Nature*, 527, 78-81.
- Kudelas, D., Kosco, J., Taus, P. (2014) The potential of utilization and evaluation of polymetallic nodules bed in clipperton-clarion locality in Pacific ocean. *International Multidisciplinary Scientific GeoConference* Surveying Geology and Mining Ecology Management SGEM.
- Kummer, J.T., Oei, D.G. (1982) A chemically regenerative redox fuel cell. *Journal of Applied Electrochemistry*, 12, 87-100.
- Kummer, J.T., Oei, D.G. (1985). A chemically regenerative redox fuel cell. II. Journal of Applied Electrochemistry, 15, 619-629.
- Li, B., Nie, Z., Vijayakumar, M., Li, G., Liu, J., Sprenkle, V., Wang, W. (2015) Ambipolar zinc-polyiodide electrolyte for a high-energy density aqueous redox flow battery. *Nature Communications*, 6.
- Linden, D. (1995) Handbook of Batteries and Fuel Cells. 2nd ed. New York McGraw-Hill.
- Menictas, C., Skyllas-Kazacos, M. (2011) Performance of vanadium-oxygen redox fuel cell. *Journal of Applied Electrochemistry*, 41, 1223-1232.
- Moraw, F., Fatih, K., Wilkinson, D.P., Girard, F. (2007) Evaluation of the Fe(III)/Fe(II) Redox Fuel Cell Cathode Couple in a Bioelectrolytic Solution. *Advanced Materials Research*, 15-17, 315-320.
- Nandanwar, M.N., Kumar, S. (2014) Modelling of Effect of Non-Uniform Current Density on the Performance of Soluble Lead Redox Flow Batteries. *Journal of The Electrochemical Society*, 161, A1602-A1610.
- Oei, D.G. (1982) Chemically regenerative redox fuel cells. Journal of Applied Electrochemistry, 12, 41-51.
- Patterson, S., Gold, R. (2018). There's a Global Race to Control Batteries—and China Is Winning. *The Wall Street Journal*, February 12, 2018.
- Pellegri, A., Spaziante, P.M. (1983) Redox process and accumulator. CA1143432 A1 patent application.
- Pissoort, P.A. (1933) *Storage batteries*. FR754065 patent application Copyright (C) 2016 American Chemical Society (ACS). All Rights Reserved.
- Pletcher, D., Wills, R. (2004) A novel flow battery: A lead acid battery based on an electrolyte with soluble lead(ii) Part II. Flow cell studies. *Physical Chemistry Chemical Physics*, 6, 1779-1785.

- Ponce de León, C., Frías-Ferrer, A., González-García, J., Szánto, D.A., Walsh, F.C. (2006) Redox flow cells for energy conversion. *Journal of Power Sources*, 160, 716-732.
- Potash, R. A., McKone, J. R., Conte, S., Abruña, H.D. (2016) On the Benefits of a Symmetric Redox Flow Battery. *Journal of The Electrochemical Society*, 163, A338-A344.
- Putt, R.A., Attia, A. (1982) Development of zinc bromide batteries for stationary energy storage. Rolling Meadows, IL: Gould, Inc.,.
- Savinell, R.F., Liu, C.C., Galasco, R.T., Chiang, S.H., Coetzee, J.F. (1979) Discharge Characteristics of a Soluble Iron-Titanium Battery System. *Journal of The Electrochemical Society*, 126, 357-360.
- Skyllas-Kazacos, M., Chakrabarti, M.H., Hajimolana, S.A., Mjalli, F.S., Saleem, M. (2011) Progress in Flow Battery Research and Development. *Journal of the Electrochemical Society*, 158, R55-R79.
- Skyllas-Kazacos, M., Rychcik, M., Robins, R.G., Fane, A.G., Green, M.A. (1986) New all-vanadium redox flow cell. *Journal of the Electrochemical Society*, 133, 1057-8.
- Skyllas-Kazacos, M., Peng, C., Cheng, M. (1999) Evaluation of Precipitation Inhibitors for Supersaturated Vanadyl Electrolytes for the Vanadium Redox Battery. *Electrochemical and Solid-State Letters*, 2, 121-122.
- Takaya, Y., Yasukawa, K., Kawasaki, T., Fujinaga, K., Ohta, J., Usui, Y., Nakamura, K., Kimura, J.I., Chang, Q., Hamada, M., Dodbiba, G., Nozaki, T., Iijima, K., Morisawa, T., Kuwahara, T., Ishida, Y., Ichimura, T., Kitazume, M., Fujita, T., Kato, Y. (2018) The tremendous potential of deep-sea mud as a source of rareearth elements. *Scientific Reports*, 8, 5763.
- Tauš, P., Taušová, M., Šlosár, D., Jeňo, M., Koščo, J. (2015) Optimization of energy consumption and cost effectiveness of modular buildings by using renewable energy sources. Acta Montanistica Slovaca, 20, 200-208.
- Thaller, L.H. (1976) *Electrically rechargeable REDOX flow cell*. US 3,996,064 patent application 3,996,064.
- Ulaganathan, M., Aravindan, V., Yan, Q., Madhavi, S., Skyllas-Kazacos, M., Lim, T.M. (2016) Recent Advancements in All-Vanadium Redox Flow Batteries. *Adv. Mater. Interfaces*, 3, 1-22.
- USGS. (2017) Production of vanadium https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/mcs-2017-vanad.pdf [Online]. Available: https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/mcs-2017-vanad.pdf.
- Vanýsek, P. (2015) From the Editor: The Fall of the Falling Mercury. *The Electrochemical Society Interface*, 24, 3.
- Vanýsek, P., Chladil, L., Dvořák, P. (2015) Velké srovnání metod a systémů uchovávání energie. Dostupně a schůdně. *HW server*, 1-8.
- Vesborg, P.C.K., Jaramillo, T.F., (2012) Addressing the terawatt challenge: scalability in the supply of chemical elements for renewable energy. *RSC Advances*, 2, 7933-7947.
- Wei, X., Cosimbescu, L., Xu, W., Hu, J.Z., Vijayakumar, M., Feng, J., Hu, M.Y., Deng, X., Xiao, J., Liu, J., Sprenkle, V., Wang, W. (2015) Towards High-Performance Nonaqueous Redox Flow Electrolyte Via Ionic Modification of Active Species. *Advanced Energy Materials*, 5, 1400678.