Redox Flow Battery: System for test series with recycling material

T Hickmann[1, *] and *O* Zielinski[1]

[1] Eisenhuth GmbH & Co. KG, Friedrich-Ebert-Straße 2013, 37520 Osterode, Germany

Abstract. In this paper a system for experiments on redox flow batteries is presented, giving the operator the possibility of dealing independently with advantages and challenges of this innovative energy converter, in particular with regard to testing new, in this case recycled, materials. The recycling aspect is included due to the permanent requirement of reducing cost of especially as far as bipolar plates is concerned. In addition the hole recycling discussion, it is necessary to use the material recycling in different stages of system development and evaluation. Included in the tests was the development of a four-part series of experiments, in the framework of which the operators will treat intensely the cell structure, its characterization as well as testing of the electrolytes and the challenge of the crossover.

1 Introduction

Modern energy systems, such as redox flow batteries (RFB), recently are becoming increasingly popular in the specialist trade [1–5]. Despite a number of demonstrative tests on redox flow batteries [4–7], up to now there does not exist a system that configures structure, functioning and challenges of real redox flow batteries by tests. In this paper a redox flow battery is presented. The goal has been the development of a series of tests by which testers and scientists may develop by independent experiments in various stages an understanding of the technical, physical and chemical bases of redox flow batteries. Moreover, also complexities or challenges respectively of this technology, such as tightness of the cell or crossover effects, shall be imparted. Thus, the users may get a differentiated and critical picture of this future-oriented technology in order to increase their own evaluation competence.

2 Process

The origin of redox flow batteries goes back to investigations and processes for the storage of electrical energy in liquids. These investigations took place in the midst of the 20th century by Walther Kangro and Heinz Pieper at the Technological University of Braunschweig[8–10], having been taken up again by NASA in the 1970ties [11]. The All-Vanadium-RFB has been investigated intensely in the 1980ties by Maria Skyllas-Kasacos et al. of the Australian University of New South Wales [12] and patented in 1988 [13]. It is at present the most thoroughly investigated and most widely distributed redox flow battery. Due to the quest for renewable energies and the search for new storage technologies, the redox flow batteries as a promising, efficient and cost-effective alternative for the storage of big quantities of electrical energy recently experience a sort of renaissance.

2.1 Principle of the redox flow battery

As far as the existing networks are concerned, their controllability becomes more and more difficult and the provision of a continuous, uninterrupted energy supply more uncertain. A remedy to this only can be the expansion of storage technologies. Electrochemical systems in the form of rechargeable batteries seem to be a promising technology. The redox flow battery is an already well-developed technology. In the case of a redox flow battery, the active material consists of salts dissolved in a liquid electrolyte. Redox flow batteries work with an electrolyte tank for each of the two electrode sides. At charging and discharging, the oxidation stage of the dissolved ions of the salt is modified. Of the up to now known ionic systems, the version with V^{2+}/V^{3+} (negative pole) and V^{5+}/V^{4+} (positive pole) in sulfuric acid is the technically most promising variant as no permanent damage will be caused by the transition of ions from one electrode side to the other side, which up to now cannot be avoided, but produce only gradual power losses. This results in an energy storage system appropriate also for long-term use.

The electrolyte is stored in tanks and forwarded in case of need to a central reaction unit for the charging or discharging process by pumps. As the solubility of the vanadium salt in the sulfuric electrolytes normally is not very high, only energy densities within the range of the lead-acid battery are reached, a fact, however, that constitutes no decisive negative aspect for stationary storage. Normally the central reaction unit

* Corresponding author: t.hickmann@eisenhuth.de

consists of two porous electrodes separated by a membrane. The tank options for the storage of electrical energy define the capacity of the battery, the size of the charging/discharging unit the power out- and input of the battery.

Safety advantages have to be highlighted, in comparison with other storage batteries, e.g. lithium bases systems which show a significantly higher danger potential due to the high reactivity of the lithium, the inflammable organic solvents and the high energy. In comparison, the aqueous electrolytes of the redox flow battery based on vanadium are not inflammable but rather environmentally harmful. In the following equations are shown the reactions occurring in the battery during discharge.

On the positive electrode:

$$V^{5+} + e^- \rightarrow V^{4+} \tag{1}$$

or

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O \tag{2}$$

On the negative electrode:

$$V^{2+} \rightarrow V^{3+} + e^- \tag{3}$$

Summary reaction:

$$V^{2+} + VO_2^+ + 2H^+ \rightarrow V^{3+} + VO^{2+} + H_2O \tag{4}$$

At charging, the reactions will occur in opposite direction.

3 Results and discussion

It has been the goal of the project to develop a series of tests which will give scientists the possibility to experience advantages and challenges of redox flow batteries by own tests and to test materials. The objective was to select from the great number of possible and already characterized systems a functioning system appropriate for the scientific field.

3.1 The test setup of the cell

The test setup was provided by Messrs. Eisenhuth GmbH & Co.KG. The cell, from inside to outside, consists of the diaphragm fixed between two plastic frames of polypropylene (PP). As membrane, the cation exchanger diaphragm was used which has a thickness of 50 mm.

The electrolytes are distributed by the plastic frames with an effective surface of abt. 28 cm^2 so that they maintain a good contact with the diaphragm and the electrodes. Downstream, a graphite felt for extending the electrode surface as well as the proper graphite electrode are located, from which the electric power can be taken via a current spoon of copper. Between the frame plates of PVC, the setup is held together via ten screws and sealed by various gaskets. Basically it will be possible to joint several cells to form a stack.

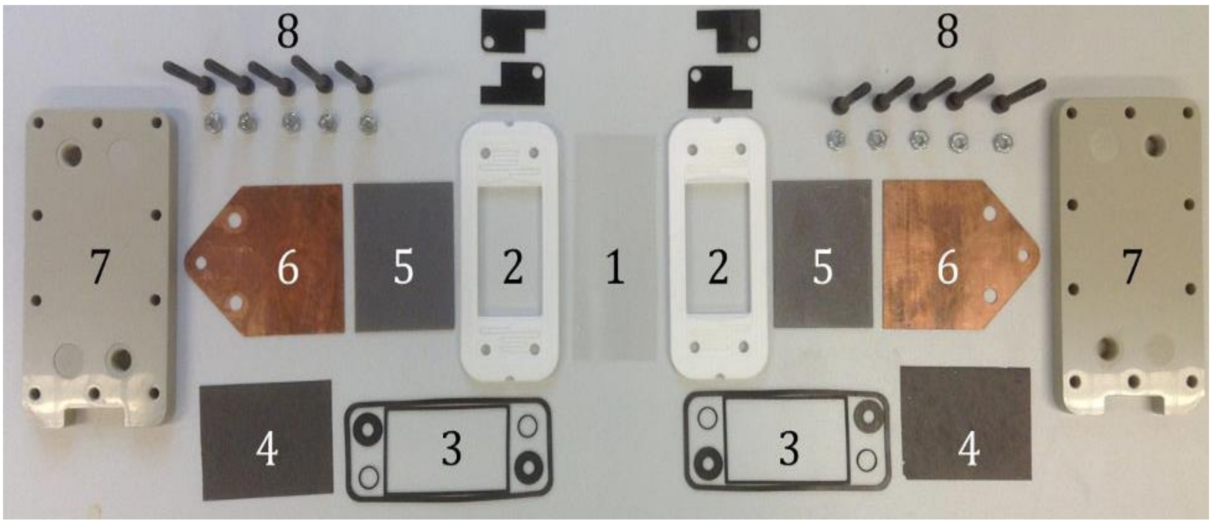

Figure 1 Structure of the redox flow battery from inside to outside: 1) Diaphragm 2) Plastic frame 3) Gaskets 4) Graphite felt 5) Graphite 6) current spoon of copper 7) Outer frame of PVC 8) Screws and nuts.

3.2 Characterization of the cell

By an exemplary test of an alternative electrolyte based on Iron a 20 minutes charge by 1.2 V and a pumping speed of 11 mL/min resulted in charging currents of nearly 100 mA and a following idle voltage (open-circuit voltage OCV) of abt. 830 mV. Besides that, certainly the battery will be suitable for optimizing the flow speed and the concentrations of the electrolytes. On the other side, the redox flow battery herein presented deliberately has not been designed for efficiency and high energy densities but shall serve scientists as means for recognizing possibilities and challenges of this technology by tests.

3.3 Usage of recycling materials

The raw material graphite was counted since the year 2010 among the 14 raw materials critical for the European economy. This is due, on one side, to the great demand by the high-tech industry and on the other side due to the high supply dependency, as up to 95% of the natural graphite are imported from China. Therefore, the safe supply to the European industry since 2010 has to be considered as potentially critical, for proving the possibilities and challenges of this technology by testing.

In parallel to the shortage of the raw materials, the Vanadium-RFB technology has to compete for cost and technology with other technologies, in particular with the lithium ion storage technology. Against this background, it is more than advisably to look out for alternative materials. Also Messrs. Eisenhuth, who investigates together with a consortium alternative material sources, in particular from the recycling sector, are confronted with this task.

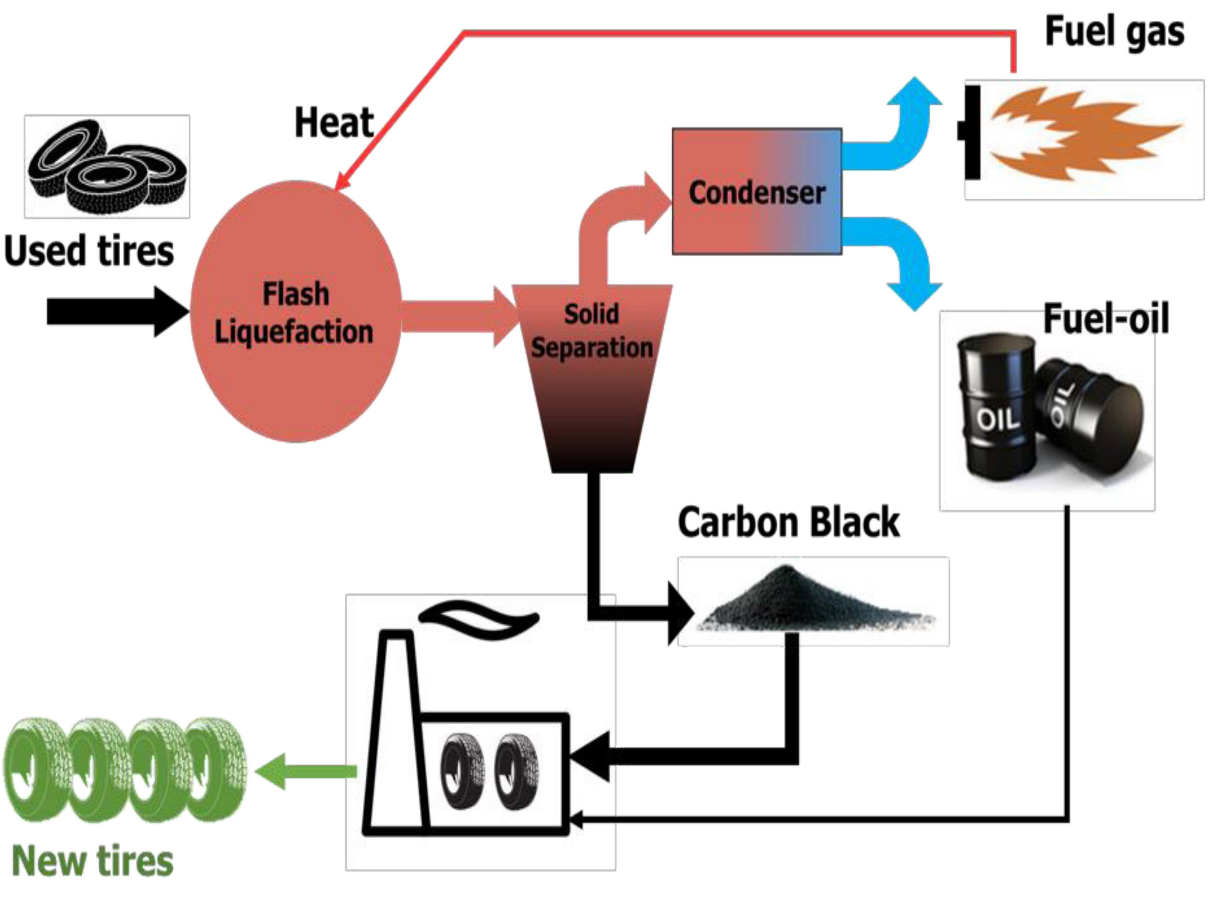

Figure 3 Principle of producing carbon black and graphite from used tires

In this connection, the production of carbon black and graphite from used tires is an interesting option. In this case the suitability of the recycling materials in different ways produced, as regards their purity, is investigated. The test series preferably are carried through by the above-mentioned test system, which can be assembled quickly and integrated easily into the system.

4 Conclusion

The recycling components produced can be manufactured easily and cost-effective and can be integrated without any problems into a redox flow test system. For the testing system, the corresponding characteristics, such as charge and discharge, can be measured immediately. Besides that, the test system is very well suited for testing corresponding small quantities of materials. Therefore, this system is also used for the test series of recycling material. As a next step it is worth to consider other materials such as the frame or the Membrane in order to decide to use recyclable material.

The authors thank the German Federal Ministry of Economy (BMWI) for financial support (project No. 03ET6050A).

References

1. Skyllas-Kazacos M Chakrabarti M H Hajimolana S A Mjalli F S Saleem M 2011 Progress in Flow Batters Research and Development Journal of the Electrochemical Society 158 (8) pp R55–R79.
2. Weber A Z Mench M M Meyers J P Ross P N Gostick J T Liu Q 2011 Redox flow batteries: a review Journal of Applied Electrochemistry 41 pp 1137–1164
3. Noack J Roznyatovskaya N Herr T Fischer P 2015 The Chemistry of Redox-Flow Batteries Angew. Chem. Int. Ed. 54 pp 9776–9809
4. Quarthal D Novotyn, J Oetken M 2017 Farbspiel in Redoxflussbatterien, Nachrichten aus der Chemie 65 pp 672–675
5. Rosenberg D Pansegrau S Wachholz M Rehling A Busker M Jansen W 2017 Redox-Flow-Batterien – Organische Batterien mit Zukunftsperspektiven CHEMKON 24 pp 325–340
6. Medienpaket der Siemens-Stiftung zum Thema „Kondensator, Wasserstoff, Redox-Flow – Wir speichern regenerative Energie“ (https://medienportal.siemensstiftung.org/portal/main.php?todo=showObjData&objid=104350, 18.09.2017)
7. Hempelmann R 2015 Redox-Flow-Batterie. In: Mischnick P Deusing-Gottschalk I (Hrsg.) Chemie und Energie – Was gibt es? Was ist zu tun?, Druck- und Verlagshaus Zarbock GmbH & Co.KG Frankfurt pp 38–39
8. Kangro W 1954 Verfahren zur Speicherung von elektrischer Energie Patent DE914264 veröffentlicht am 28. Juni 1954
9. Pieper H 1958 Zur Frage der Speicherung von elektrischer Energie in Flüssigkeiten Dissertation Technische Hochschule Braunschweig
10. Kangro W Pieper H 1962 Zur Frage der Speicherung von elektrischer Energie in Flüssigkeiten Electrochimica Acta 7 (4) pp 435–448
11. Thaller L H 1975 Energy storage system Patent US3996064 veröffentlicht am 7. Dezember 1976
12. Skyllas-Kazacos M Rychcik M Robins R G Fane A G Green M A 1986 Journal of The Electrochemical Society 133 (5) pp 1057–1058.
13. Skyllas-Kazacos M Rychick M Robins R G 1988 All-vanadium redox battery United States of America Patent