Organic Redox Flow Batteries: An Innovation in the Field of Education for Sustainable Development for Educational Curricula

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Abstract
Wind, solar and other renewable energies are intermittent energy sources. For example the availability of electric power from solar plants depends on the amount of available sunlight. Hence renewable energy sources generate electrical power in the case of solar power plants according to the availability of sunlight and in case of wind generators according to the weather depending availability of wind. For this reason the increasing amount of power from renewable energy sources has to be combined with innovative energy storage systems. Due to the expansion of power generation from renewable sources, there is a need for more and more flexible, efficient energy storage systems.
Redox flow batteries are discussed as a possible energy storage system to solve this problem mentioned above. All redox flow batteries use different redox couples as reacting species. Liquid electrolyte solutions of the reacting species flow through the electrochemical cells during charge and discharge. Up to now different metal ion couples like vanadium and iron have been investigated. In addition, redox flow batteries which make use of organic redox couples like quinones and hydroquinones are discussed.
In this article we present an experimental set-up that can be used to demonstrate the functionality of redox-flow-batteries to students. Therefor different everyday life chemicals are used as redox couples. At the end we also discuss how to use these organic redox flow batteries in the field of education for sustainable development in school curricula and in extra-curricular settings.

1. Introduction
In the last few years the amount of renewable energy sources (e.g. wind or solar energy) in electrical grids increased. But the availability of solar energy depends on the available sun light and also the availability of electric power from wind turbines depends on the wind offered by nature. Solar, wind and other renewable energies are intermittent energy sources. In consequence with an increasing amount of renewable energy sources the amount of intermittent energies increases, too. Hence innovative, appropriate and flexible energy storage systems with high capacities are needed to guaranty a stable electric grid. Such innovative energy storage systems which are discussed at the moment are so called flow batteries.

2. Theoretical Background: Flow Batteries
In flow batteries water soluble redox couples are used. The substances of one redox couple is solved in an aqueous electrolyte. Hence an electrolyte in which one redox couple is solved flows through one half cell of the flow battery. During charge or discharge the reacting species is reduced or oxidized in the flow battery. Afterwards the electrolyte can be stored in tanks. Therefore such flow batteries have a high capacity [1].
The idea of this setup of flow batteries and research on proper redox couples is already established. For example the NASA developed in the 1970ies flow batteries with the redox couple Fe^{2+}/Fe^{3+} in the one half cell and the redox couple Cr^{2+}/Cr^{3+} in the other half cell. Further different redox couples with vanadium-ions in different oxidation stages (e.g. V^{2+}/V^{3+} and VO^{2+}/VO_2^{+}) have been developed successfully. In addition, semi-flow-batteries based on the redox couple Zn/Zn^{2+} have been investigated [1, 2]. Different industrial companies test flow batteries with vanadium-ions at the moment.

Further organic redox couples may be appropriate substances for redox flow batteries. Aziz et al. [3,4] and Narayanan et al. [5] investigate redox couples of quinones and hydroquinones in redox flow batteries. Both research groups use carbon electrodes. Aziz et al [3,4] utilize in one half cell 9,10-anthraquinone-2,7-disulfonic acid solved in sulfuric acid and in the other half cell bromide-ions solved in water. While charging the battery 9,10-anthraquinone-2,7-disulfonic acid is reduced to 9,10-anthrahydroquinone-2,7-disulfonic acid (figure 1) and bromide is oxidized to bromine.

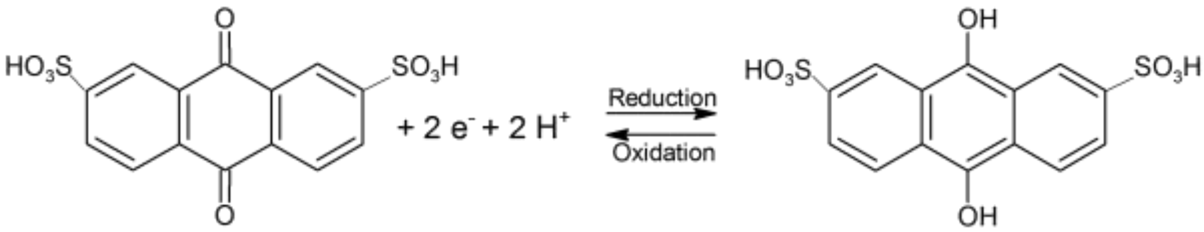


Figure 1: Reduction of 9,10-anthraquinone-2,7-disulfonic acid and oxidation of 9,10-anthrahydroquinone-2,7-disulfonic acid

Terminal voltage of the electrochemical cell results in 1,0 V. Current density is about 0,95 A cm^{-1} to 2,25 A cm^{-1}. Further the flow battery shows high cycle stability.
Narayan et al [5] utilize 1,2-benzoquinon-3-5-disulfonic acid instead of bromine. While the battery is charging 1,2-benzoquinone-3,5-disulfonic acid is oxidized to 1,2-benzoquinon-3,5-disulfonic acid (figure 2).

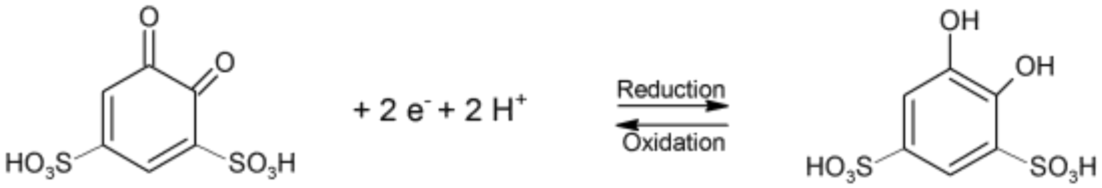


Figure 2: Reduction of 1,2,benzoquinone-3,5-disulfonic acid and oxidation of 1,2-benzohydroquinone-3,5-disulfonic acid

An 9,10-anthrahydroquinon-2,7-disulfonic acid / 1,2,benzoquinone-3,5-disulfonic acid electrochemical cell shows a terminal voltage of 0,74V. The cycle stability of this flow battery is high, too.

3. Demonstration of flow batteries in science lessons

In conclusion flow batteries are a current and important theme in the context of renewable energies. Hence flow batteries should be implemented in science curricula at school. Therefore we present experiments and models to demonstrate the functionality of flow batteries in chemistry lessons. We developed experimental setups which are as simple as possible. In order to this in an experiment it can be shown, those organic compounds could be used in batteries. In these experiments in one half cell of the battery an organic redox couple is used. In the other half cell we use an oxygen-consuming electrode. Hence the current of the battery is more stable and a small electric motor can be driven for quite a long time. In this set-up of organic battery the organic substance is oxidized in one of the half cells and oxygen is reduced in the other.

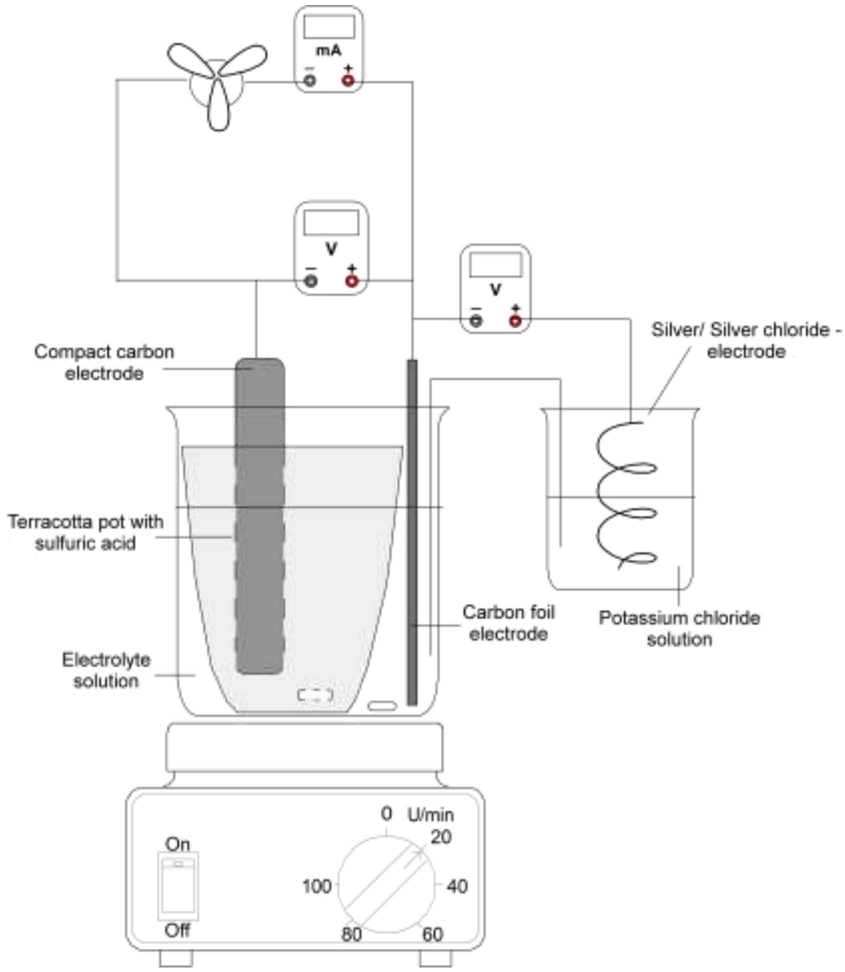
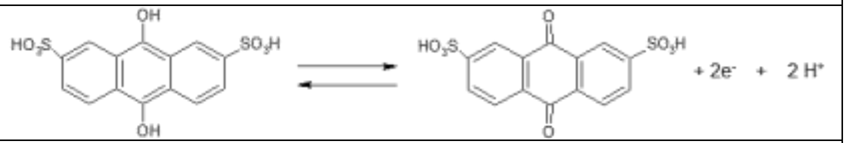
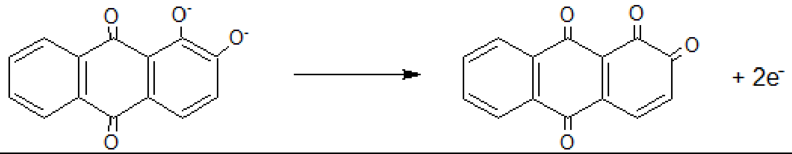
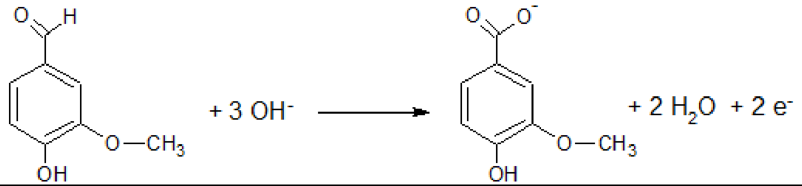
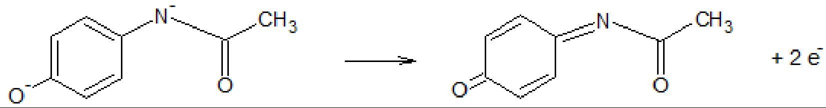
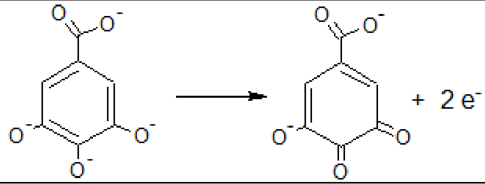


Figure 3: Experimental set-up of an organic redox battery

An experimental set-up as shown in figure 3 is used. The reaction vessel is a 600mL beaker. An electrolyte in which the redox couple is solved is given into the beaker. A clay pot which is filled with sulfuric acid stands in the beaker. The clay pot is used as semipermeable membrane. A carbon electrode (carbon film) hangs in the electrolyte with the organic substances. A self-made porous carbon electrode which is made out of a carbon stick, activated carbon a perforated sleeve (available in home improvement centers) [6] hangs in the sulfuric acid. A better result can be achieved if sodium peroxydisulfate is given to the sulfuric acid. Sodium peroxodisulfate reacts to sodium sulfate, hydrogen peroxide and oxygen. Hence the potential is higher and more stable. With a magnetic mixer the flow in the battery can be simulated.

With this experimental set-up different organic substances can be investigated. Especially different quinones and hydroquinones can be used. First of all anthraquinonedisulfonic acid can be used to construct a battery. Therefor anthraquinonedisulfonic acid is solved in sulfuric acid (c=1 mol/L). In addition different chemicals of everyday life, especially quinones or hydroquinones of everyday life can be used as organic reactive species. For example, vanillin (e.g. in vanillin sugar), paracetamol (e.g. in medicine), alizarin (e.g. as a natural dye) and gallic acid can be used. These organic substances are solved in sodium hydroxide (c=1 mol/L). In table 1 an overview of exemplary organic substances which can be used is given. Further the oxidation of the different organic substances and the terminal voltage of the organic battery are mentioned.

Table 1: Exemplary organic substances that can be used in organic batteries

Organic compound	Terminal voltage	
anthrahydro-quinone-disulfonic acid	1,0 V	
alizarin	1,1 V	
vanillin	1,0 V	
paracetamol	1,08 V	
gallic acid	1,3 V	

According to [3,4,5] a battery using the redox couple anthrahydroquinonedisulfuric acid/ anthraquinonedisulfuric acid can be discharged and afterwards charged again. In case of redox batteries using alizarin, vanillin and paracetamol discharging the battery is possible. Charging these batteries again is not possible. Up to now it isn´t clear if a battery with gallic acid can be charged again. Hence further research (e.g. cyclovoltammetry) is needed.

4. Flow Batteries in science curricula

The shift from nuclear and coal-fired power plants to renewable energies is a current and important theme of modern society. Hence flow batteries are an authentic, actual problem in the context of sustainable development. The UNESCO called out the years from 2005 to 2014 as a worldwide decade for education in sustainable development [7]. Sustainability is a special term, which is often used in the field of environmental education. But education for sustainable development is an advancement, which involves also the ecological perspective and additional the economic and social dimension [8]. In view of change to renewable energies and their storage, students will be confronted with this topic in the future. This is important for the educational part, to develop this issue and new experiments in curricula. The demonstration of flow batteries can give an effort to education for sustainable development. Furthermore this material could be used in extra-curricular settings (e.g. science labs) [9]. In future, a new science lab will be started at the University of Flensburg. The lab will focus on education for sustainable development. The presented material in the field of organic redox flow batteries will available for students to explore.

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