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Topics for Teaching: An Energy Storage System and its Phenomenological Approach

Hybrid Flow Batteries Based on Ink Cartridges with Spectacular Colour Changes

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Abstract: The following article shows how a simple construction of a hybrid flow battery can be realised with medical technology materials. The implementation of this future-oriented topic is an example of a curricular innovation and should already be included in school curricula, since future generations will have to deal intensively with the energy transition (not only in Germany) and renewable energies. An electrolyte based on ink cartridges was used to motivate the pupils. The use of this 'everyday chemical' creates a real life reference for the students in the classroom, which can increase the popularity of chemistry teaching.

Keywords: Chemical education · Colour changes · Energy storage systems · Flow batteries · Ink cartridges

On the popularity scale of pupils, chemistry is rather stuck in the midfield. Over the school years, its popularity decreases steadily and reaches its lowest point in the higher classes. The reason for this is the constantly increasing difficulty of the subject through the increased use of quantitative calculations, model-like considerations and the use of chemical symbols.[1] In summary, chemistry lessons become more and more abstract for the students and must therefore be made more motivating. This can be achieved by linking chemistry lessons to the pupils' environment by dealing with research-relevant and everyday topics.[2] Redox flow batteries represent such a topic relevant to everyday life, especially since, for example, the energy transition was decided in Germany in 2011.

There is an increasing need for stationary storage systems, which temporarily store the energy from fluctuating regenerative energy sources to make it available again during dark periods. The special feature of redox flow batteries is that the energy is stored in liquids, which are pumped from a tank into the energy converter during the charging process, where they are then oxidised/reduced and returned to the tank again. This process continues until the electrolytes are completely oxidised/reduced. The electrolyte which is oxidised during discharging is called the anolyte and the electrolyte which is reduced is called the catholyte.[3]

The construction of redox flow batteries is quite complex for the classroom, therefore so-called hybrid flow batteries can also be built, in which zinc sheets can be used as the anode material instead of an additional electrolyte. With the help of medical technology materials, a graphite felt (*https://www.sglcarbon.com/pdf/SGL-Datasheet-SIGRACELL-Battery-Felts-EN.pdf; type GFA 6 EA*) and a pump (*https://www.conrad.de/de/p/modelcraft-kraftstoff-getriebepumpe-benzinfest-foerdermenge-0-6-l-min-207894.html*), an efficient electrolyte flow can then be generated, as well as a suitable ratio between graphite surface and catholyte volume. This is necessary to convert the electrolyte (catholyte) in a moderate time and thus make a colour change of the electrolyte perceptible at the phenomenological level. Due to different colours of the electrolyte in the oxidised/reduced state, the battery's state of charge can easily be seen by the students.

To assemble the hybrid flow battery (Fig. 1), the following steps must be performed: First, two tiny holes are made in a 60 ml plastic syringe (approx. at the 15 ml & 35 ml markings). Then a piece of graphite felt (4 x 19 cm) is cut out and rolled up as closely as possible along the long side. This graphite felt roll is inserted into the syringe with the help of the plunger and pushed to the end of the syringe. For the electrical contacting of the graphite felt, an approx. 4 cm large piece of a pencil lead is inserted through the prefabricated hole at the end of the syringe. At the height of the second hole, a zinc sheet – formed into a ring – can be pushed into the syringe. Here, too, a piece of a pencil lead is pushed through the hole to fix the zinc ring for electrical contact. It must be taken care that the zinc ring and the graphite felt do not touch, otherwise the battery will short-circuit. The only things missing are two so-called extension lines (type Heidelberger, length: 30 cm; *https://www.bbraun.com/en/products/b/extension-line-typeheidelberger.html*). These are connected to the syringe and to the pump in such a way that the electrolyte is later forced to run through the graphite felt from above.

One question that remains is how to use hybrid flow batteries in a motivating way in chemistry classes. Both in Germany and

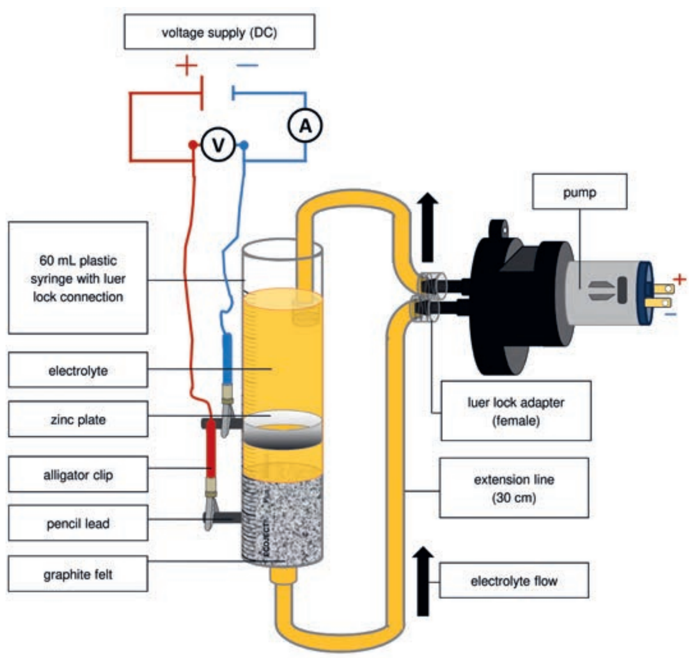


Fig. 1. Experimental setup of a hybrid flow battery.

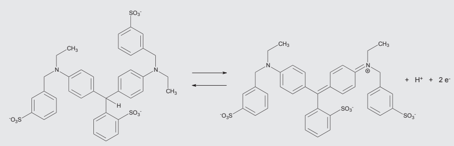
in Switzerland, the curricula of the higher classes demand that students acquire the competence to explain the possibilities and problems of electrochemical storage of energy in batteries.[4–6] Baden-Wuerttemberg's (DE) curriculum specifies that teachers should ensure that they include everyday life- and previous experiences of the pupils in their lessons to acquire the required competences. In addition, special emphasis should be placed on the use of everyday chemicals in class.[4] While experimenting with flow batteries, it turned out that several triphenylmethane dyes, *e.g.* Brilliant Blue FCF are suitable for use in these energy storage devices. While searching for everyday products containing these dyes, the authors came across commercially available ink cartridges, among other things. In almost every stationery shop one will find various ink cartridges of common companies (Pelikan, Lamy, …). The use of these cartridges results in particularly impressive electrolyte colours depending on the state of charge, but it must be added that for these purposes Lamy's colours (Fig. 2) are even more suitable than those of Pelikan (Fig. 3). For each coloured electrolyte, 100 ml of a 1 M $ZnSO_4$-solution is prepared, and a complete ink cartridge is dissolved in it.

The two pictures (Fig. 2 & 3) show the discharging process of such flow batteries based on ink cartridges. The subsequent charging processes lead back to the original colour, whereby it must be taken care that the voltage is not applied too high (1.6–2 V), otherwise the dyes could be destroyed.

During the discharging process, elemental zinc is oxidised to Zn^{2+}-ions (Eqn. (1): ←), while the dye contained in the ink cartridge is reduced (Eqn. (2): ←). The reduction and the associated addition of a hydrogen ion to the dye molecule cause the system of delocalised electrons to be interrupted. The central C-atom has four single bonds and is thus sp^3-hybridised. The conjugated double-bond system is interrupted, the electrons can no longer be distributed over the entire molecule and the substance loses its colour because it can no longer interact with visible light. Therefore, the electrolyte usually appears almost colourless after discharging. The reaction equations during a charging or discharging process are formulated as an example for the dye Brilliant Blue FCF, which has in solution such a blue colour as the Pelikan ink cartridge in Fig. 3. The forward reaction represents the charging process (→), the backward reaction the discharging process (←):

– pole: $$Zn^{2+} + 2\,e^- \rightleftarrows Zn \quad (1)$$

+ pole:



(2)

Methodologically reduced, the reaction equation (Eqn. (3)) for the dye Brilliant Blue FC (BB FCF) is as follows:

+ pole: $$\text{BB FCF}_{(red.)} \rightleftarrows \text{BB FCF}_{(ox.)} + H^+ + 2\,e^- \quad (3)$$

However, the most impressive ink cartridge in terms of colour is the Lamy T10 Neon Lime. It contains the same dye as highlighters: pyranine. The electrolyte is additionally acidified with sulfuric acid, so that due to the increasing protonation of the sulfonic acid groups the dye fluoresces blue (Fig. 4, right) after a discharging process (←) under UV light. As soon as the hybrid flow battery is recharged (→), the fluorescence disappears, and the electrolyte is coloured yellow (Fig. 4, left) under daylight. During the charging process, Zn^{2+}-ions are reduced to elemental zinc (Eqn. (4): →), while the dye contained in the ink cartridge is oxidised (Eqn. (5): →). The forward reaction represents the charging process (→), the backward reaction the discharging process (←):

– pole: $$Zn^{2+} + 2\,e^- \rightleftarrows Zn \quad (4)$$

+ pole: $$x\ \text{Pyranine}_{(red.)} \rightleftarrows x\ \text{Pyranine}_{(ox.)} + x\,e^- \quad (5)$$

blue fluorescent yellow

In summary, for use in school, it can be said that the teachers themselves are free to choose the colour they prefer. However, the authors recommend the use of the fluorescent ink cartridge, as it adds another interesting component that is spectacular for students. In addition, this system seems to be the most reversible. Ideally, the hybrid flow batteries based on ink cartridges should have already been discharged once, because the very first discharging process takes a little longer for all colours, regardless of the manufacturer.

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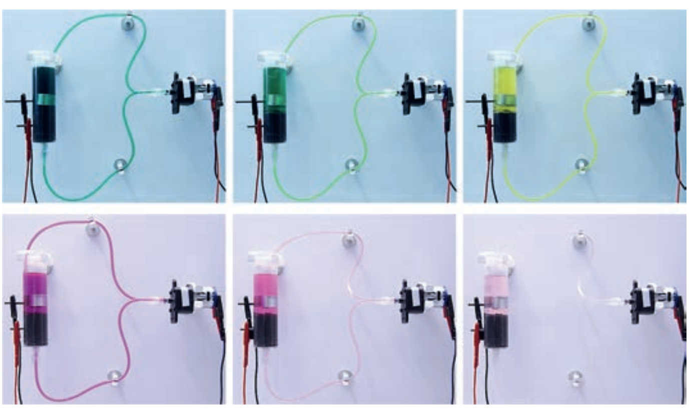

Fig. 2. Top: Discharging Lamy T 10 Green in 1 M $ZnSO_4$; bottom: discharging Lamy T 10 Violett in 1 M $ZnSO_4$.

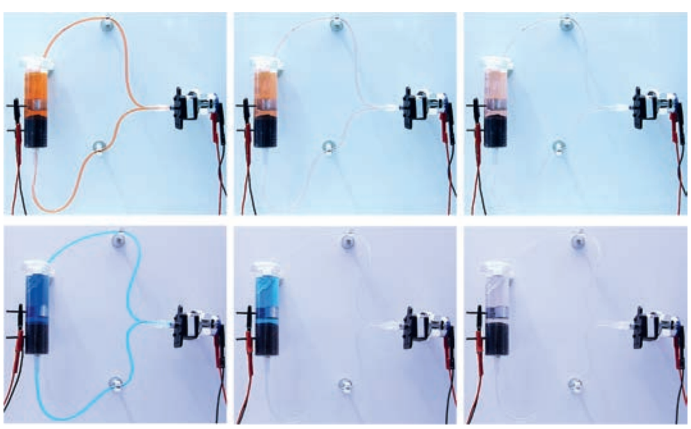

Fig. 3. Top: Discharging Pelikan TP/6 4001 Brilliant Red in 1 M $ZnSO_4$; bottom: discharging Pelikan TP/6 4001 Turquoise in 1 M $ZnSO_4$.

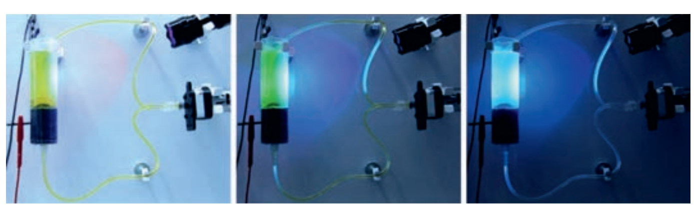

Fig. 4. Left: Start of discharging process of Lamy T 10 Neon Lime in acidified 1 M $ZnSO_4$ under daylight; middle: during discharging under UV light; right: completely discharged hybrid flow battery under UV light.

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