Bio-based electrolytes for redox-flow-batteries

S. Ravichandran, B.O. Burek, J. Schuster, C. Weidlich, K.-M. Mangold, J.Z. Bloh
e-mail: bloh@dechema.de
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Introduction

With further progress in the conversion of our energy production towards more inherently volatile renewable energy sources (solar, wind, etc.) there will be an increased demand in storage capabilities, up to TWh in scale. Besides other storage technologies such as pumped hydro and compressed air storage, redox-flow-batteries present an appealing opportunity. A flow battery is technically akin both to a fuel cell and an electrochemical accumulator cell (electrochemical reversibility). Since the energy is stored in liquid electrolytes, this battery type can very easily be scaled up by just using a larger electrolyte tank.

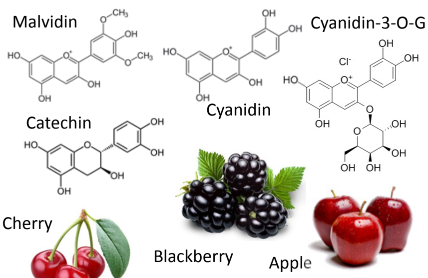
The All Vanadium redox-flow-battery is the current state of the art. For this kind about 3 kg vanadium/kWh energy capacity are required [1]. The worldwide production of vanadium is about 60 *kt* per year [2]. So even using the whole global vanadium production, only about 20 GWh worth of storage capacity could be build. This simple calculation shows that there are likely significant vanadium supply problems, if these batteries are to be built on a TWh scale.

Aim

Organic redox active substances are an alternative solution to Vanadium [3,4]. Anthraquinones, anthocyanes and flavonoids are in this case the object of desire. These substances can be found in the nature and yield from renewable raw materials. For example rhubarb and senna contain anthraquinones. The redox potential is about 0,2 V vs. *RHE* (Reversible Hydrogen Electrode) and is well suited as an analyte for *RFB*. Anthocyanes and flavonoids can be found in grapes, apples, cherries etc. The redox potential of anthocyanes and flavonoids is about 0.9 V vs. *RHE* and can be used as an catholyte. Those electrolytes can replace the poisonous and highly corrosive vanadium electrolytes [5]. With this combination of bio-catholyt and -anolyte it is possible to realize a completely bio-based redox-flow-battery.

The highest concentration of various redox active substances can typically be found in the shells of fruits. During the production of wine and juice very large amounts of pomace accumulates. The aim of the project is to extract redox active compound rich mixtures from these fruit residues and use cyclic voltammetry to determine their redox potential and reversibility.

Anthocyanes & Flavonoids



Extraction Method

An aqueous two-phase system published by Hua [6] was used to extract anthocyanins and anthraquinones present in the fruit residue or fruit peel. This extraction system consisted of 30% (w/w) ethanol and 20% ammonium sulphate with a ratio of material and solvent of 1:20. The extraction mixture was treated by vortexing for 30s, ultratorax for 30s and ultrasound for 30s and then allowed to stand at room temperature for 30 min. After that it was centrifuged at 4 °C at 4000 RPM for 15 min to facilitate phase separation. The top phase was collected and the ethanol evaporated. Finally the raw extract was freeze-dried.

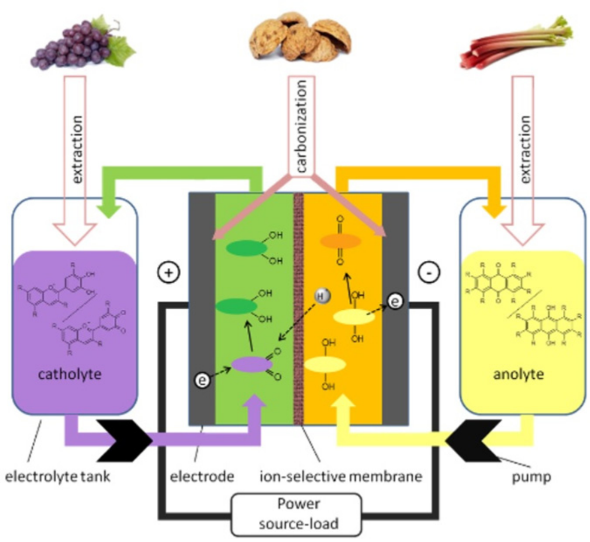
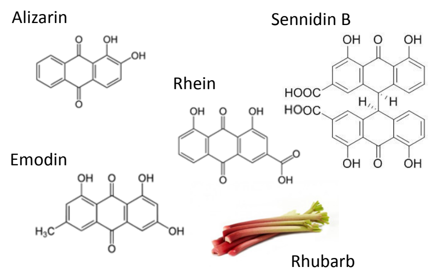


Fig. 1: Schematic illustration of bio-based redox-flow-battery.

Anthraquinones



Yield of Extraction

Tab. 1: Results of extraction by Hua[6]

Fruit / Vegetable	Yield [%]
Apple	28
Cherry	34
Blackberry	38
Rhubarb	15

Results

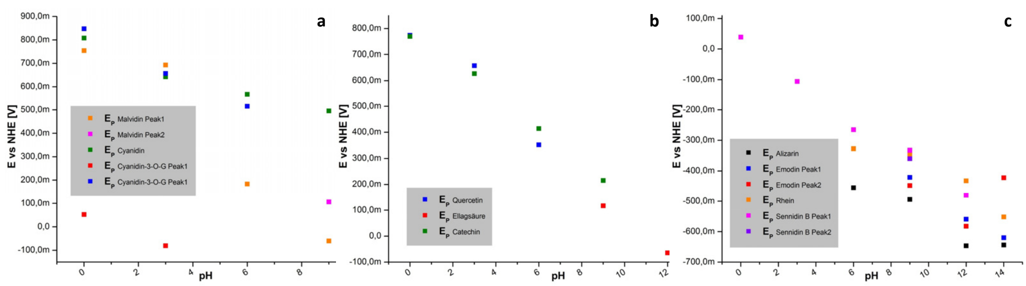


Fig. 2: Redox potential vs pH for anthocianines (a), flavonoids (b) and anthraquinones (c).

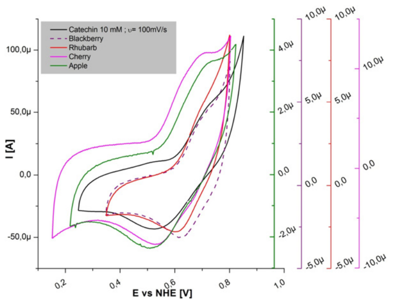


Fig. 3: Redox potential of 2 g/L raw flavonoid extracts from several fruits at pH 3; u = 50 mV/s.

Conclusion

- Cyclovoltammetric measurements have shown reversible redox behaviour of Anthocyanes, Flavonoids, and Anthraquinones.
- With the combination of anthraquinones as anolyte and anthocyanes as catholyte it is possible to achieve a bio-based redox-flow-battery with estimated nominal voltage of 0.8 V.

Outlook

- Determine the power density of redox active substances and extracts
- Measure the nominal voltage of future bio-based batteries
- Evaluate carbonized biomaterial as bio-based electrodes
- Find ideal biomass waste streams to use
- Compare and optimize different extraction methods
- Study the long-term performance and storage capacity of the bio-based electrolytes

Literature

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