

The Compbat project has reached its last year yet, therefore interesting results start to be achieved, in this second newsletter you can get a grasp of the main research activities and achievements of the groups involved in the project.

“High-throughput screening methodology”, Research Centre of Natural Sciences-TTK (Hungary):

The TTK team is currently expanding the molecular library of redox active compounds beyond the pyridoxal database. The main aim is to build a structurally diverse set of molecules using the developed computational protocol, and apply machine learning techniques for high-throughput screening of the target 100 000 molecules.

The TTK team is primarily involved in work package WP1, which aims at developing a high-throughput screening methodology that enables the identification of promising candidates of water-soluble compounds for new generation redox flow batteries. The group has developed an efficient computational protocol that utilizes a combination of various electronic structure methods and it provides high quality predictions for reduction potentials. The protocol has been applied to build a molecular database comprising over 6700 pyridoxal-based molecules.

Several machine learning (ML) techniques, including the commonly used random forest algorithm as well as graph convolutional neural networks, were applied to the pyridoxal database to assess their performance for predicting reduction potentials and aqueous solubilities. Most of the tested ML methods were found to perform remarkably well, exceeding the accuracy of the quantum chemical computational protocol used to generate the pyridoxal database.

Some of the pyridoxal derivatives examined computationally were synthesized by the JYU group, but stability problems were encountered in electrochemical studies. To provide insight into the stability issue, the TTK group adopted a new computational methodology for the characterization of radical stabilities, and provided a detailed analysis for the entire pyridoxal molecular set (see Figure below). The radical stability descriptors were found to be rather sensitive to the bulkiness of the substituent at the pyridinium N atom, as well as to electronic

and steric nature of the other substituents. The radical forms of the compounds synthesized within work package WP4, were predicted to be unstable species.

Current activities of the TTK team are focused on the expansion of the molecular library of redox active compounds beyond the pyridoxal database. A molecular library of viologen derivatives is being developed, and a structurally very diverse set of molecules from open access databases are compiled. The application of the high-throughput screening methodology elaborated within CompBat will enable the screening of about 100 000 molecules.

Here we include a figure that illustrates the stability analysis of pyridoxal derivatives (see below).

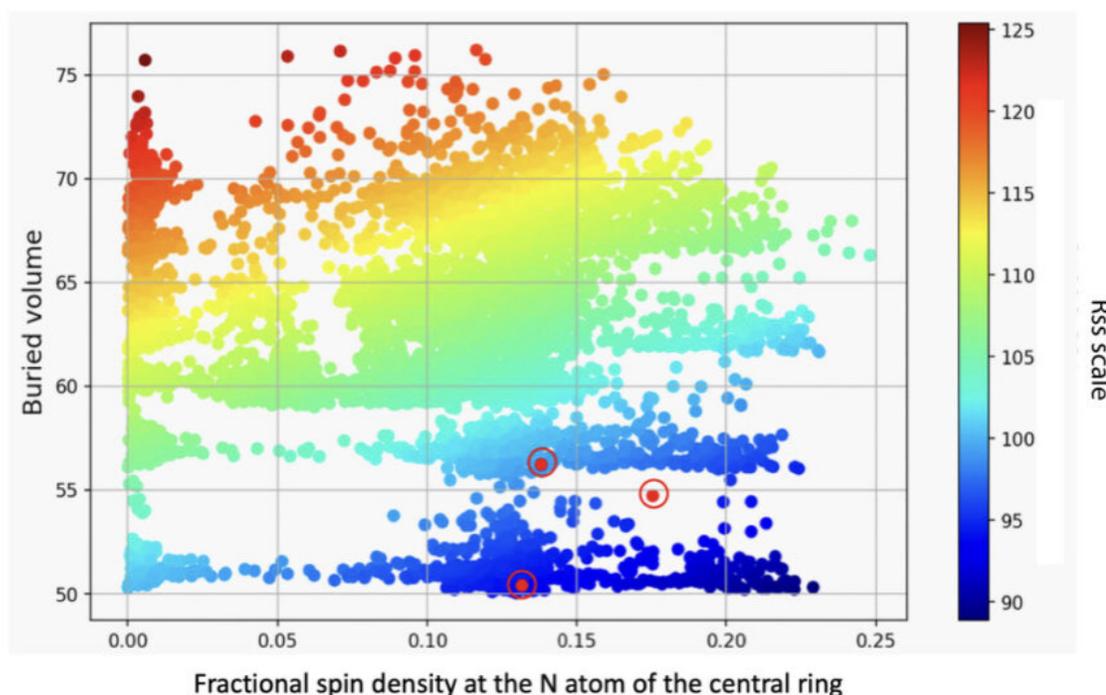
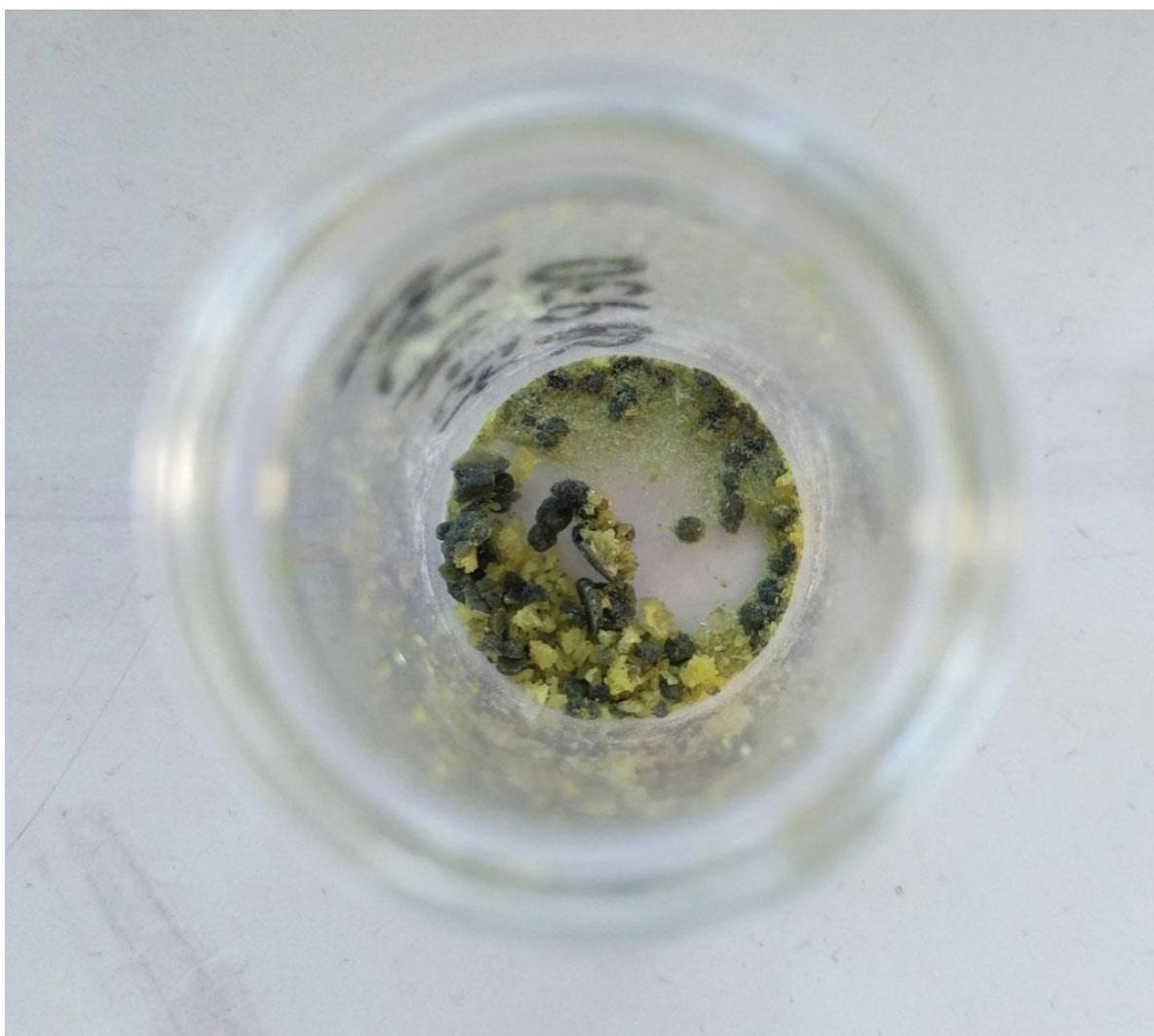


Figure shows the computed radical stability data for the entire set of radicals included in pyridoxal database. Color scale is used for *radical stability score (rss)* data (blue – unstable, red – stable radicals). The circled red dots in the middle-bottom refer to the compounds synthesized within CompBat.

“Towards bioinspired battery materials derived from vitamins”, Jyväskylä University (Finland):

The Pihko group at Jyväskylä University (JYU) focuses on the chemical synthesis of new materials that could be utilized to store energy in flow batteries. We start from natural products, such as vitamins, that possess the requisite properties as starting materials for the synthesis. After several chemical steps and purifications, we then arrive at chemically modified molecules that will then be tested whether they are going to be stable in the chemical reactions that take place in the battery. We have recently identified a key molecule that appears to possess the necessary qualities and are now exploring improved routes for the chemical synthesis as well as simpler versions of the molecule.



As shown in the figure, the newly synthesized materials are solids and readily dissolve in water. Work is underway to improve their purification and scaling up the synthesis. So far, the JYU team has made an interesting breakthrough in the chemical synthesis of bioinspired molecules for redox flow batteries, within the CompBat project. We have now identified a pyridoxal-based molecule that appears to be stable over 50 redox cycles in aqueous media, but at present only at high pH. The key to this success lies in protecting one of the anionic groups in the molecule – without this protection, the molecules were unstable irrespective of pH. We are currently expanding on this finding with newly designed molecules that retain the protective group but include groups that should be stable in lower pH. The current hypotheses behind the stability issues will be put to test with these new materials.

A relatively robust synthetic route to these water-soluble flow battery materials has been developed, and JYU is currently also engaged in scaling up the production from milligram to gram scale. Several bottlenecks and setbacks in the synthesis have been identified and the problems have been circumvented. We have also provided materials for the electrochemical testing of the synthesized materials, in collaboration with the University of Turku (UTU) team. These experiments have provided important and decisive feedback and they will now guide our synthetic efforts as they have provided key data on the stability of the materials under different conditions. Furthermore, leveraging upon the abovementioned work, additions to the sets of molecules identified in the first CompBat WP was possible expanding it including new molecules based on the current hypotheses for stability.

“Model the kinetics of electrochemical redox reactions at the electrode-electrolyte interface”, Aalto University (Finland):

We use quantum mechanical constraint density functional theory (CDFT) in combination with ab initio molecular dynamics (AIMD) to model the kinetics of electrochemical redox reactions at the electrode-electrolyte interface. Marcus theory is used to couple two states of reactant and product with electron transfer kinetics. We also study the resulting kinetics of reactions between some organic redox active molecules as anolyte and graphene as electrode. All these molecules undergo consecutive electrochemical reactions with one electron being transferred at each stage. This theoretical study contributes towards the development of a realistic-level prediction of electron transfer kinetics suitable for energy storage applications.

LUMI supercomputer used for the Aalto simulations.

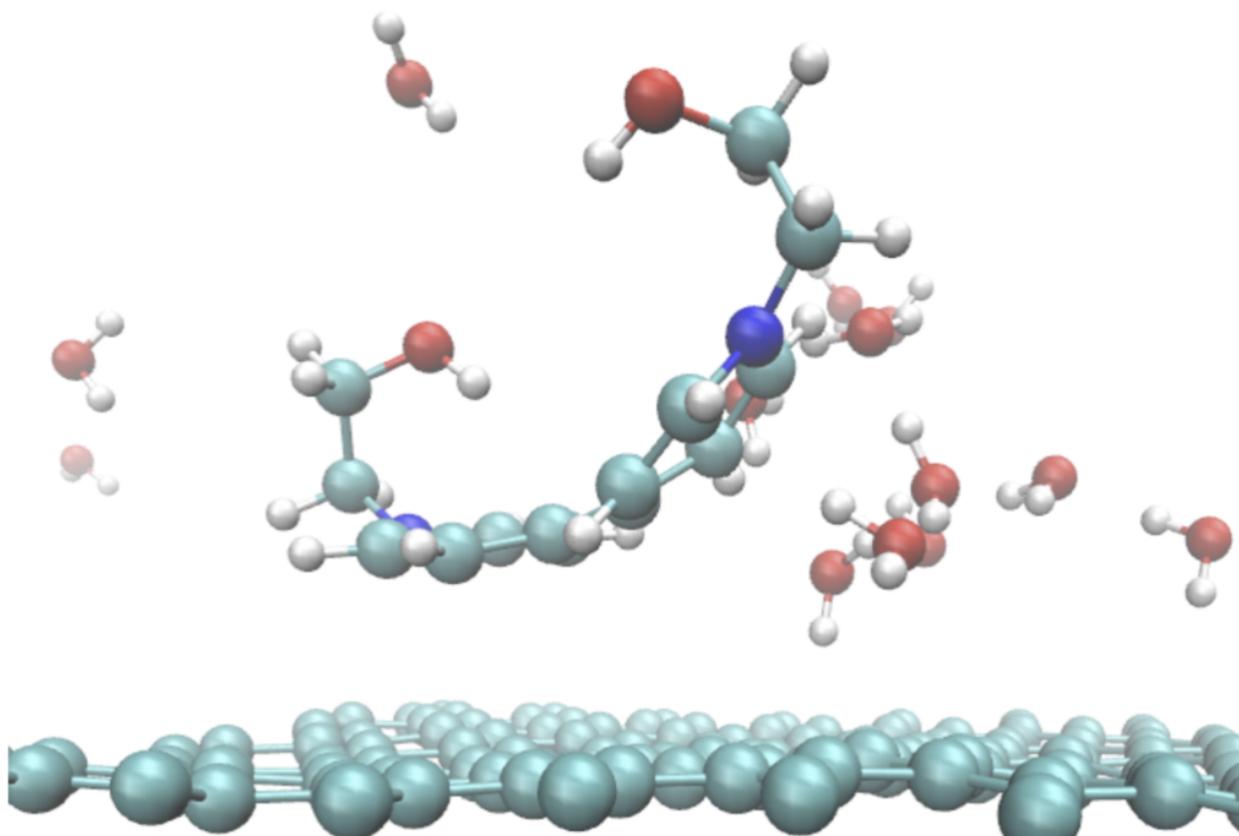


By introducing a two-state system of reactant (i) and product (f), Marcus theory (MT) estimates the interfacial electron transfer (ET) rate constant, which is a key parameter for analyzing the kinetic reactions during the charging and discharging processes of RFBs. All parameters of the theory (see FIG 1) are calculated using the quantum mechanical constraint density functional theory method in combination with ab initio molecular dynamics. We model the electrode with a single layer of graphene and Methyl-viologen (Me-Vi), 6,6'-dimethyldiquat (DMDQ), desalted Basic Red (dBR5), 2-hydroxy-1,4-naphthaquinone (2HNQ), and 1,1'-di(2-ethanol)-4,4'-bipyridinium (OH-Vi) were selected for the electrolyte molecules.

The kinetics of reactions can be understood using the MT parameters listed in TABLE I. In most cases, the transfer rate is high, which is not quantitatively consistent with experiments. In general, two types of reactions are expected on the surface of the electrode. First, the molecule comes close enough to accept an electron and, in the best case, leaves the interface. Second, the molecule sticks to the surface and poisons the catalytic activity of the electrode, which is unfavorable. While the former is called an outer-sphere ET, the latter is an inner-sphere with a much higher transfer rate. Our results show that both types are possible in RFBs, depending on the nature of the components. For example, we found that dicationic viologen-based molecules are strongly adsorbed when the first electron is embarked. At the smallest distance, we expect an inner-sphere ET, which is also thermodynamically favorable.

This leads us to rethink about the realistic electrode: the electrode surface could be covered by the first few redox active molecules. This may prevent next molecules to stick to the surface. We are now investigating the distance-dependent ET on clean and molecule covered surface to see if we can find the outer-sphere reaction for viologen-based molecules.

As another example, we would like to mention, is the phenazine-based molecule. The mechanism is different because of the protonation that must be included at some stage. Our results for a pH neutral electrolyte show that both ETs are an outer-sphere with two well separated reaction potentials. We think that the second ET is probably inaccessible unless the pH is changed. Our molecular-level computational analyses and calculations can be used to study ET in detail, paving the way for future screening of larger data sets.

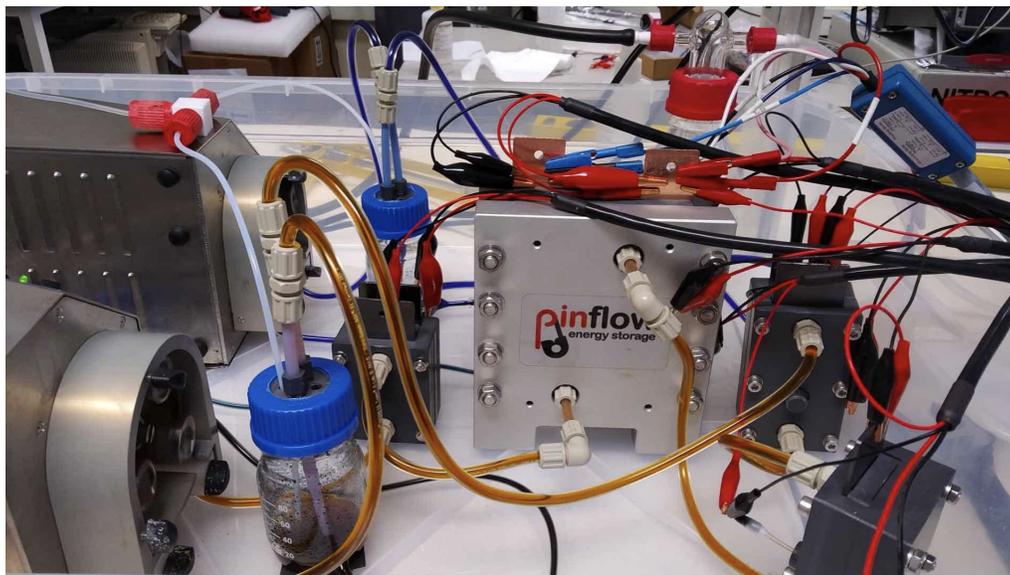


Snapshot of a simulation the OH-Viologen molecule on graphene.

“Electrochemical testing at Turku University”, The University of Turku (Finland):

Focusing on the development of Aqueous Organic Redox Flow Batteries (AO-RFBs), the experimental electrochemistry is conducted at Turku University. The group led by Prof. Pekka Peljo is carrying out the electrochemical analyses of new synthesized organic molecules as well as running lab-scale batteries to provide the experimental data needed for model's validation. The testing of the new materials ranges from the standard electrochemical analysis to the proper testing in a lab-scale RFB. Organic molecules synthesized at University of Jyväskylä are tested in Turku, firstly with cyclic voltammetry. The most promising candidates are then analyzed in a cell to check the stability, an important factor when considering organic molecules for a RFB. The picture below shows an H-cell used to run a galvanostatic cycling of one of the synthesized pyridoxal-based molecules tested at Turku University.

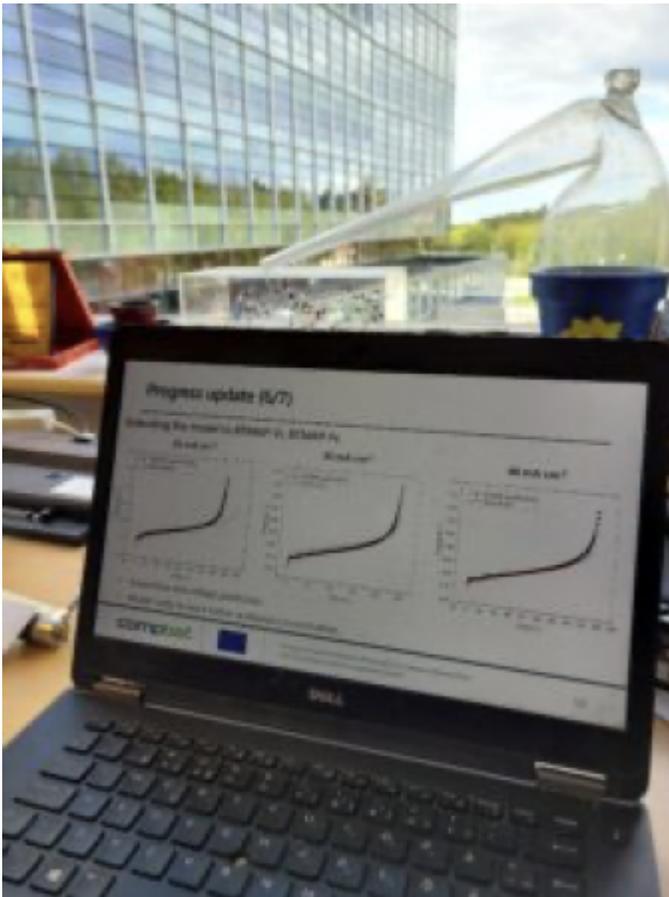
The electrochemical results obtained coupled with complementary studies, as mass spectroscopy and NMR analysis, serve as feedback to design the next new candidates. Both Universities work in cooperation in order to define the next steps to improve the performance of the new organic materials in a flow battery. Within the CompBat project, the performance of organic couples in a proper flow battery is also studied at University of Turku. The experimental set up used in this research includes additional in-situ potential measurements that allow a further analysis of the redox couples studied. This configuration provides information of the processes occurring in the battery allowing to monitor both electrolytes separately, determinate half-cells state of charge and predict possible imbalances in the system. The additional measurements are obtained using secondary cells in the system, as shown in the figure below.



So far, this system has been used to study the behavior of vanadium and other commercial organic couples. In the future, this experimental work will be extended to analyze the new synthesized materials. The results already obtained have been used to validate a zero-dimensional model for RFB simulation developed within the CompBat project with high fidelity.

“Redox flow battery and solid boosters finite element model”, Uppsala University (Sweden):

The objective of Work package 2 is the construction of a finite element model for a redox flow battery, parametrized with input data coming both from density functional theory (DFT) calculations and experimental measurement. The purpose of this model is the development of a predictive tool for conventional and solid boosted redox flow batteries with an experimental validation. This model should be able to predict the voltage and current generation. To reach these objectives, it is necessary a permanent synergy between all the WPs involved in the project.



Flow cells being simulated in front of the new Ångström building at Uppsala University, Sweden

UU contribution in the project is summarized in three tasks: multiphysics finite element flow battery model, parametric sweep and packed bed reactor model. In the first two tasks a time dependent model was constructed using the software COMSOL Multiphysics. The starting point

was a vanadium redox flow battery model in order to reproduce the main features of the electrochemical behaviour. This model combines a 2D approach for the flow cell and a 0D representation of the tank. The parameterization was carried out combining the experimental measurements with a parametric sweep.

A flexible model was created with the objective of adapting the electrochemistry to new redox species without a significative change in the computational approach. A similar study was performed for the species BTMAP-Fc /BTMAP-Vi and the results showed a good agreement with experiments.

In the third task, the proof of concept of a computational model for a packed bed reactor filled with solid boosters was developed. The computational approach combines two models, on the one hand the flow battery model aforementioned and, on the other hand, the addition of an explicit representation of the tank with a solid booster, choosing LiFPO₄ as a solid material. For the last one, the electrochemistry was studied using the Newman model for an equivalent Li-ion battery and the Butler-Volmer equations for the intercalation process in the solid material. This proof of concept has demonstrated that, despite simplifications, the addition of the solid material in the reservoir of the tank disruptively increases the battery capacity.

In the framework of the CompBat project, a detailed thermodynamic study of this kind of batteries has been published and a multiscale approach of this kind of devices is depicted in the figure below.

“Multi-cells stack system and shunt current distribution modelling”, University of Pisa (Italy):

The work performed so far within the CompBat project by the University of Pisa, with the support of all the partners, aims at modelling a multi-cells stack system of redox flow batteries (RFBs). The level of detail is a compromise between accuracy and computational burden, targeting system-level analysis of energy losses, aimed at upscaling RFB performance from single-cell laboratory experiments to stack level. The model is used to simulate multi-cells vanadium redox flow battery (VRFB) and aqueous organic redox flow battery (AORFB) systems, considering the effect of design and operational parameters on energy losses and overall performance.

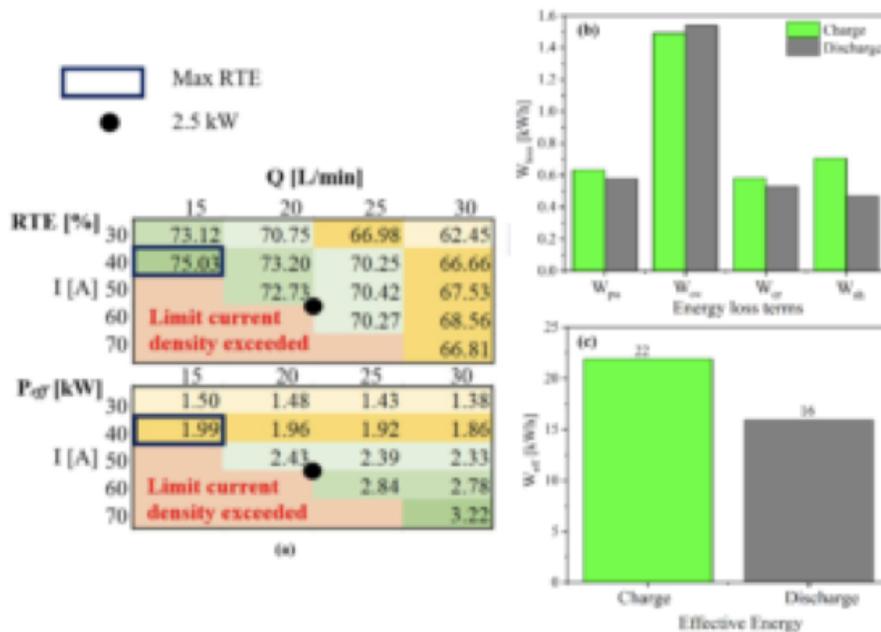
The multi-cells zero-dimensional model is used to investigate the effect of pump, shunt current, overpotential, and crossover losses, and to evaluate their contribution to total energy losses.

After validation with literature data on VRFB systems, the performance of the battery under different test cases is simulated by analysing the effect of manifold diameter, current, flow rate, tank size, electrolyte concentration, standard potential, internal resistance, and limiting current density.

Results show that these parameters contribute to overall RFB performance to varying degrees.

Decreasing the manifold diameter is found to reduce shunt current losses without significantly increasing pumping losses, thus improving the roundtrip efficiency. Also, while it is beneficial to slightly increase stack current at a small flow rate to yield more power, a trade-off between stack current and flow rate is essential.

Compared to vanadium, by using the same stack and by optimising current and flow rate, the organic system, chemical composition will be soon disclosed in scientific publications, has shown to produce less power and energy, with a roundtrip efficiency of between 50 and 60%, albeit with a comparatively lower share of shunt current losses to the total energy losses. While the energy can arguably be increased by using solid boosters, the power output needs to be enhanced by significantly reducing the area-specific resistance of the cell and, simultaneously, by increasing the limiting current density; additionally, looking for redox couples with higher open-circuit voltage is another suggested direction for research. In summary, the modelling activities enabled the understanding of critical aspects of RFB systems during their scaleup from cell to the stack level and provide a valuable tool for system design optimisation as well as for techno-economic assessments.



Here beside you can see examples of results presenting (a) the roundtrip efficiency (RTE) and effective power (P_{eff}) discharged for different values of current and flow rates (b) Breakdown of energy losses (pumping, overpotential, crossover and shunt) and (c) effective energies in the roundtrip at the nominal operating point of 2.5 kW discharge power (i.e., $I = 51.5$ A, $Q = 20.5$ L/min) during charge and discharge.

Scientific publications

Finally, a couple of scientific publications have been released so far, these are literature reviews dealing respectively with a promising way to increase the battery energy capacity, namely the solid boosters: "Thermodynamics, Charge Transfer and Practical Considerations of Solid Boosters in Redox Flow Batteries" (<https://www.mdpi.com/1420-3049/26/8/2111>), and with the battery environmental footprint: "Life cycle assessment (LCA) for flow batteries: A review of methodological decisions", (<https://www.sciencedirect.com/science/article/pii/S2213138822005094>).