Synthesis and investigation of nano-dispersed solid electrolyte systems for the design of highly efficient redox flow cells

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Bachelor thesis

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Table of Contents

0 Table of figures

1 Introduction

Nowadays, the demand of energy storage technologies is increasing considerably, due to increasing consumption and increasing population. Depending on the energy and power demand different energy storage solutions can be used, which include batteries, capacitors/supercapacitors, pumped hydropower or compressed air, among others. During the last years, batteries attracted much attention in the research field due to the high versatility that the chemistry and cell design offer. Li-ion rechargeable batteries are market dominant in many applications such as smart phones, laptops or even electric cars, since they provide high energy and power densities. However, batteries, which are suitable for electronic devices and transportation applications, are not necessarily the best option for large energy storage facilities. Li-ion batteries have major drawbacks for large energy storage facilities such as, high prices, hazardousness of raw materials, lack of recyclability and they have a limited specific power since Li-ion can just supply one electron for the electrochemical reaction.[1]

Batteries are an important topic from the environmental point of view, since the conventional fuel energy sources are responsible of big pollution problems and the price of them is increasing, a transition to the use of renewable energies is mandatory. In order to optimize the energy generated by the intermittent renewable energy sources, such as solar energy or wind energy, batteries are a key point. Currently fossil fuel power plants need to support renewable energies, because of the dramatic changes renewable energy supplies suffer depending on the weather, for example.

In order to use renewable energies with no longer fossil fuel help it is necessary to develop large-scale energy storage facilities to store energy at peak hours and release it at off-peak hours, avoiding the consumer to notice any difference. Redox flow batteries (RFB) are a promising technology for this application, since they allow a decoupling between power output and energy storage capacity. This idea is not new but recent scientific advances, such as an increase in energy density, and the necessity of large energy storage facilities made the interest in this technology to grow.[1]

1.1 Redox-flow batteries based on solid electrolyte dispersions

A conventional RFB is a set up formed by different parts, each of them with a different function in the system.[1] Figure 1 shows a scheme of this kind of cells and the following parts:

- **Energy storage tanks:** the electrolyte is contained in this part of the system, with the desired amount of REDOX active species dissolved. In a cell, there are two storage tanks, one containing the catholyte and the other containing the anolyte.
- **Power output cell**: in this part of the RFB the electrochemical reaction occurs. Normally, it is made by a highly conductive percolating structure (made of carbon, for example), which facilitate electrons to arrive to the current collector. The current collectors, located in this part as well, are responsible of receiving/releasing electrons from the active REDOX species, and send them to the device, which requires energy. A porous membrane separates the catholyte from the anolyte and it enables ions to pass through it.
- **Pumping system**: it connects the energy storage tanks with the power output cell. It has several pumps to move the electrolyte through the battery. This part of the battery has an energy consumption, which has to be taken into account in the design and development of the system. In order to develop a successful battery, which is capable to store and

provide more energy to the consumer than it is required for the pumping system, viscosity and rheological properties are determinant.

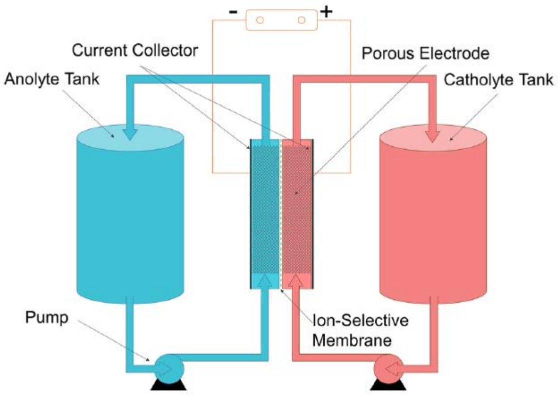

Figure 1. Common RFB scheme. [1]

In conventional RFB, during battery operation, catholyte and anolyte flow from the storage tanks to the power output cell, impulsed by the pumping system. Conventional RFB contain dissolved transition metal ions as REDOX active species, in an acidic medium. The metal ions are oxidized/reduced, depending on the operation mode (charge/discharge), while the electrolyte flows through the system and the species get in contact with the current collectors. The electrolyte is circled back to the energy storage tank after the electrochemical reaction, while the storage tank continues feeding the power output cell with new material until all the electrochemically active species of the tank are either reduced or oxidized.

On the one hand, this set up has the advantage of decoupling energy storage capacity and power output. The energy storage capacity depends on the concentration of active REDOX species in the electrolyte and the tank size, whereas the power output is by the performance of the cell, which is related the design of it and the number of cells that integrate the system.

On the other hand, the drawback that this kind of energy storage technologies suffer nowadays is the low energy densities that they offer. This lack of energy density is due to two main limitation factors, which are the solubility limit from the electrochemically active species and the narrow electrolyte stability. If the concentration of REDOX species is over the solubility limit, they precipitate and they do not have electrochemical activity anymore. In case of the electrolyte stability, a clear example is the electrolyte of the Li-ion batteries, where the dangerous and toxic part of the battery are the solvents used in the electrolyte.

Using suspensions as electrolytes and according to the goals and perspectives of the project, there are two kind of interesting systems for developing a prototype, even though other kind of set-up exist.[1] The possible strategies are the following:

- **Type I: Flowing carbon-conducting network**.

This kind of system consists in a mixed suspension based on electrochemically active and carbon particles, which would be a link between the active material and the current collector for transporting electrons. The active material stays solid during the whole charge/discharge process, and this kind of RFB have been commercialized for Li-ion as an active particle, but some literature suggest cheaper and not hazardous compounds.

The major drawback of these systems is the pump energy loss, due to the high viscosity of the fluid, research will be done in this field. The contact between the carbon and the active particles could be a limitation for the process if there are not enough collisions between them.

Using nanoparticles (NP), agglomeration has to be prevented in this kind of systems, for a better power output. It has to be said that there is a trade-off between the power density supplied and the Coulombic efficiency of the device, since when conductivity increases the shunt currents increase as well, and therefore a loss of Coulombic efficiency appears. Find an approximate diagram of this kind of system in Figure 2 (I).

- **Type II: Flowing active material particles colliding on current collectors without carbon.**

The system is very similar but the elimination of carbon from the suspension decreases the viscosity of the fluid, thus decreasing the energy required for pumping and, achieving an energy saving for keeping the liquid flowing. Without carbon the redox reaction would only occur when the active particles collide with the current collector, this is the reason for low electrochemical activity in absence of flow. The carbon withdrawal decreases the suspension conductivity as well, so an optimization process could be required for balancing viscosity (minimize the pumping energy) and conductivity of the fluid (maximize the electrochemical reactions).This kind of set-up has been tested with Li-ion and polymer suspensions. The materials required for this kind of cells need features such as high electronic and ionic conductivity.

An improvement of the energy efficiency, energy density and power output is required. One possibility is to improve the electronic and ionic transport and reduce the viscosity through surface modification. The design of the current collector might also be crucial since it should be designed to facilitate the contact with as many NP as possible while pressure drop is minimized. A schematic representation is showed in Figure 2(II).

Taking into account the positive and negative aspects of both RFB types, an interesting option would be to use an intermediate system. This would combine the use of electrochemically active particles grown on carbon.

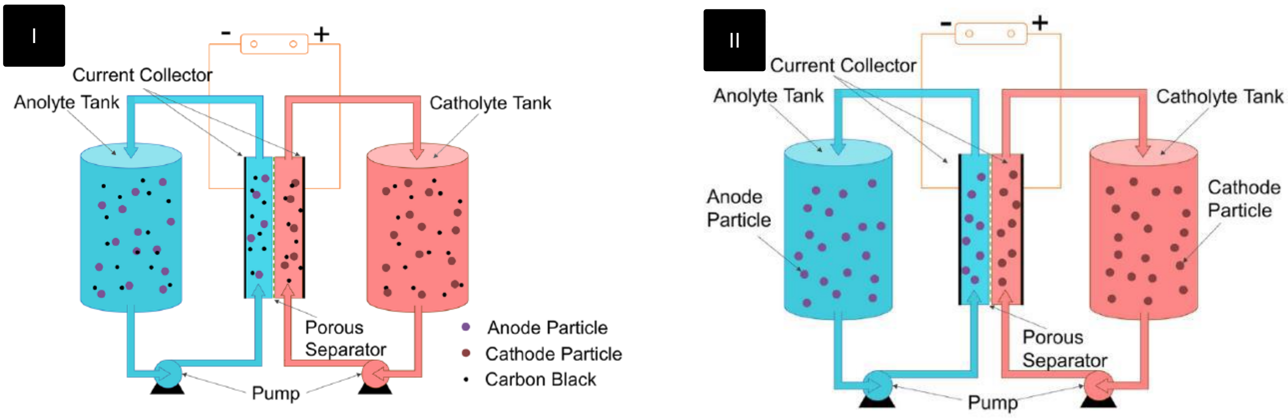

Figure 2. I) Type I: Flowing carbon conducting network; and II)Type II: Flowing active material particles colliding on current collectors without carbon. [1]

1.2 Idea of the project

The main idea of the project is to develop a semi-solid electrolyte, where suspended nanoparticles (NPs) act as the active species, which stay solid during the whole charge/discharge process. Electrons would be released/gained from the NPs in the REDOX process, when they suffer a collision with the current collector or other particles with high electronic conductivity, which would increase the electronic transport in the cell. This process is called particle-electrode impact events (PEI).[2] The project must stick to this idea, since Aigys patented this technology. This approach allows to overcome the solubility limit of the REDOX active species. Therefore, higher storage capacity would be achieved, loading the electrolyte with as much NPs as possible. Many articles and prior studies suggest that carbon particles or structures increase the electrolyte conductivity drastically.[3][4] However, other challenges arise from this approach.

The new challenges that must be faced with this novel battery design are the dispersion stability, viscosity and conductivity of the electrolyte.[1] It is required to optimize these parameters, which are strongly linked between them, to achieve the best performance of the battery. Obviously, it is required to select electrochemically active NPs, which would be a key point as well. Several researchers are investigating different kind of materials, but in this project, substances as environmentally friendly as possible were studied.

Dispersion stability is an important parameter to control, in order to avoid sedimentation of the solid content, which would provoke a loss in the battery performance. The higher the solid content the easier that this occurs. Therefore, surface chemistry would be useful in order to prevent attractive interactions between the particles and keep them as separated as possible using electrostatic repulsion interactions, sterical limitations or other intermolecular interactions.[1][2][5] Electrolyte's electric conductivity should be has high as possible to release/receive electrons in PEI easier.

Table 1 shows a summary of the most important challenges that need to be overcome to obtaining a high performance RFB, by optimizing the electrolyte. Challenges will be faced by the different collaborating entities.

Key concepts	Electrochemical activity	Viscosity	Solid content	Conductivity
High RFB performance	High	Low	High	High

Table 1. Summary table about semi-solid RFB challenges.

1.3 Part of the project belonging to FHNW

The proposed Bachelor Thesis is going to be focused on finding a promising NP dispersion with high-stabilized solid content and electrochemical activity. The inorganic nanoparticles used for the RFB must have electrochemical activity and would be bought or synthesized, depending on the price and the synthesis complexity. The electrical conductivity of the electrolyte will be studied and improved adding carbon structures, as suggested in literature and previous studies performed by partner institutions.

1.4 Inorganic materials

Regarding the possible use of transition metals, several possibilities could be found such as Pb, Fe, Cd or Mn. Most of these materials had a redox couple, which involved an ion of the same material going into solution.[1] Although, using specific conditions and material combinations dispersions could be achieved, for the use of semi-solid RFB, as explained hereinafter.

Literature about lead acid batteries reports that Pb can be used as an interesting active material acting as a negative electrode. Mesoporous carbon particles (MPC) were developed with Pb grafted in the porous, being the active part. This grafting method would prevent crystallization of $PbSO_4$ in the anode, which was the main problem of this kind of batteries, provoking a loss in the unit operation of the system after every cycle. Pb on MPC was the most promising structure, among different structures tried. However, toxicity of Pb has to be taken into account and even more for a large-scale energy storage target.[1][6]

Some authors observed the good performance of $Ni(OH)_2$ nanoplates and FeO_x nanoparticles in combination with multiwall carbon nanotubes (MWCNT) and graphene, respectively. The set-up commented resulted in an ultra-fast battery, which achieved complete charging in 2min and took 30s to discharge, providing more than 120 Wh/kg as energy density. $Ni(OH)_2$ nanoplates on MWCNT were used as a cathode and FeO_x NP on graphene was the anode.[3] Although this technology is promising, no reports about the active-carbon particles could be found. Using other carbon structures for the development of suspensions, where the active particles are attached to carbon, could be used for increasing conductivity of the fluid.

However, the possibility of using iron oxides in a basic medium does not require any species going into solution. Furthermore, iron oxides are cheap and easily available, power could be generated out of roast. Research done by several authors reported the great electrochemical activity of Fe_2O_3 NP, where the redox couple would be Fe(III)/Fe(II),acting as an anode.[7] With these NPs it was achieved a high solid content and relatively low viscosity functionalizing the NPs' surface. After the surface functionalization, with a near-monolayer coverage, the electrochemical activity was not dramatically modified. Furthermore, the dispersion was stable during 2 weeks, when the surface was modified. However, this design had no additives in the fluid for increasing conductivity or decreasing viscosity.[2]

1.5 Complex organic compounds

This kind of materials offer advantages, such as less toxicity, cheaper costs or the design flexibility (Redox potentials), and disadvantages like membrane crossover when the organic molecules are dissolved, which provoked less capacity and a loss of operating lifetime, over some inorganic materials. For solving the membrane crossover it has been reported the use of Redox active colloids (RACs) as active materials. This approach consisted in the synthesis of xPVC through emulsion polymerization as a backbone of the electrochemically active particles.[1][8] Using this idea it was possible to develop a working RFB prototype using low RAC concentration achieving coulombic efficiency around 94% at 43 $\mu A/cm^2$.[1][8] Although RACs are promising, there are drawbacks and limitations, such as that the use of this idea would mean to add particle inert additives for the suspension elaboration to avoid the membrane cross-over. Moreover, the reported solid content was low and sedimentation occurred. This approach would increase the viscosity of the semi-solid electrolyte drastically, for a few active redox couples, which would get into solution anyways. The second observed limitation the low energy density provided, which would still be a problem even increasing the RAC content in the electrolyte. Thirdly, more research would be needed in the field of gravimetric and volumetric capacity of this technology, by finding out other RAC materials with lower molecular weight. Among other challenges, the explained examples are the major drawbacks for this kind of electrolyte composition.

Literature about polyaniline (PANI) for using them in RFB as active materials. Those organic compounds have a backbone function and involves Cl^- addition/subtraction. The advantage of these polymers is its high electronic conductivity, low cost, environmental stability and good redox reversibility. Zn-PANI battery systems have been reported, with promising features. However, these provide low voltage efficiency and there are reactions, which imply dissolving compounds.[1][9]

1.6 Surface modification

For an increase in solid content surface modification of the electroactive nanoparticles is necessary, in order to produce a highly stable electrolyte suspension. However, adding molecules to the surface of the active particles implies and additional difficulty for the electron to be released at the current collectors when PEI occurs. For this reason, it is very important to choose a molecule that would stabilize the suspension and let electrons through at the same time. Suspension